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Inoue et al.

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(54) **EXHAUST PURIFICATION SYSTEM OF INTERNAL COMBUSTION ENGINE**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 162 days.

This patent is subject to a terminal disclaimer.

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(Continued)

(58) **Field of Classification Search**
None
See application file for complete search history.

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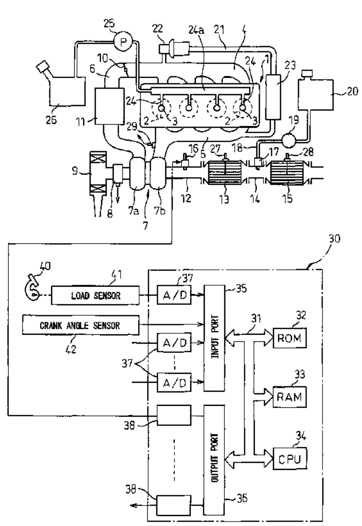
Primary Examiner — Walter D Griffin
Assistant Examiner — Jelitza Perez
(74) *Attorney, Agent, or Firm* — Oliff PLC

(57) **ABSTRACT**

In an internal combustion engine, inside of an engine exhaust passage, a hydrocarbon feed valve (**16**), an exhaust purification catalyst (**13**), an aqueous urea solution feed valve (**17**), and an NO_x selective reduction catalyst (**15**) are arranged in that order. A first NO_x purification method which makes the concentration of hydrocarbons flowing into the exhaust purification catalyst (**13**) vibrate by within predetermined ranges of amplitude and period to reduce the NO_x contained in exhaust gas in the exhaust purification catalyst (**13**) is normally used. A second NO_x purification method which uses the fed aqueous urea solution to reduce the NO_x in the NO_x selective reduction catalyst (**15**) is used when the fed hydrocarbons exceed the allowable value.

12 Claims, 17 Drawing Sheets



(51) **Int. Cl.**

F01N 3/08	(2006.01)
F01N 3/20	(2006.01)
F01N 9/00	(2006.01)
F01N 13/00	(2010.01)
B01J 37/02	(2006.01)
B01J 23/40	(2006.01)
B01J 23/58	(2006.01)
B01J 23/63	(2006.01)
B01D 53/94	(2006.01)

(52) **U.S. Cl.**
CPC ***B01D53/9477*** (2013.01); *B01D 2251/2067* (2013.01); *B01D 2251/208* (2013.01); *B01D 2257/404* (2013.01); ***F01N 3/0842*** (2013.01); ***F01N 3/0871*** (2013.01); ***F01N 3/2066*** (2013.01); ***F01N 9/00*** (2013.01); *F01N 2240/30* (2013.01); *F01N 2900/0412* (2013.01); *F01N 2900/0422* (2013.01); *Y02T 10/47* (2013.01); *Y02T 10/24* (2013.01); ***F01N 13/009*** (2014.06); ***B01J 37/0244*** (2013.01); ***B01J 23/40*** (2013.01); ***B01J 23/58*** (2013.01); ***B01J 23/63*** (2013.01); ***F01N 3/208*** (2013.01); *F01N 2610/03* (2013.01)

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Aug. 7, 2013 Notice of Allowance issued in U.S. Appl. No. 13/262,865.

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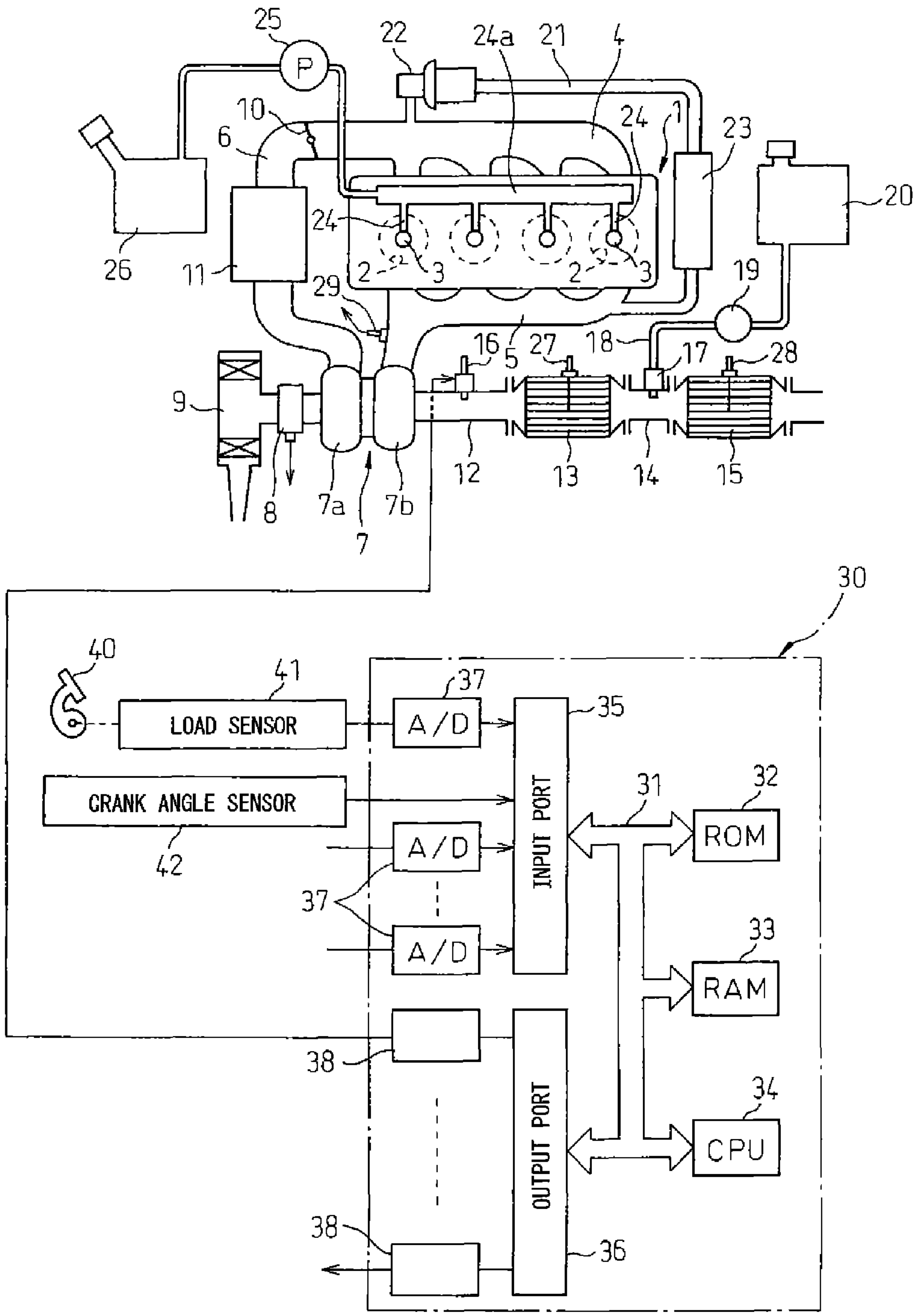
Fig.1



25
P
22
24a
21
4
10
6
24
1
23
20
26
11
24
2
3
2
3
29
19
16
27
18
17
28
5
9
8
7a
7
7b
12
13
14
15
30
40
41
LOAD SENSOR
37
A/D
35
CRANK ANGLE SENSOR
INPUT PORT
31
32
ROM
42
A/D
37
A/D
33
RAM
38
OUTPUT PORT
34
CPU
38
36

Fig. 2

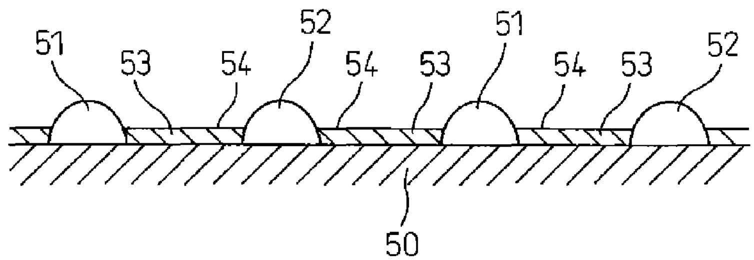


Fig. 3

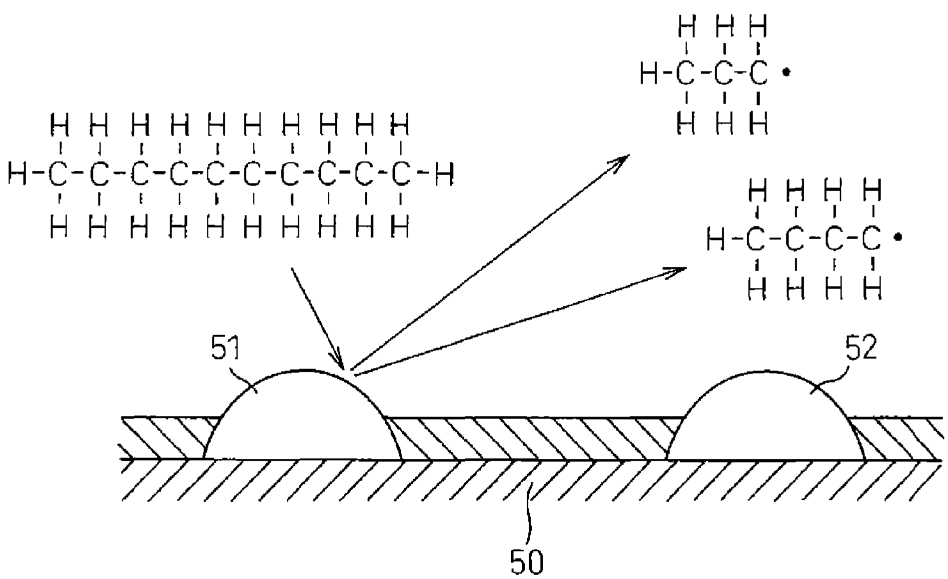


Fig.4

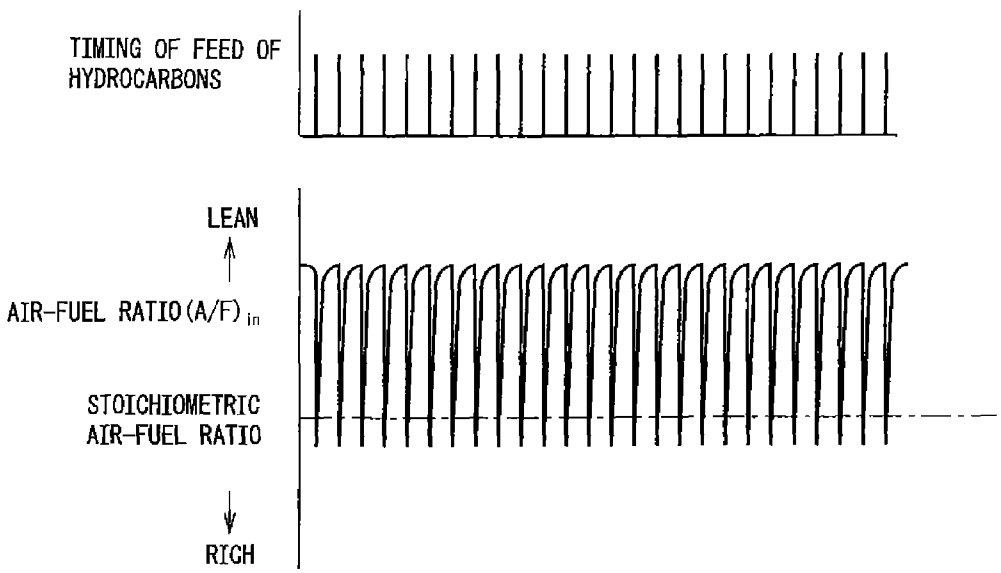

TIMING OF FEED OF
HYDROCARBONS
LEAN
AIR-FUEL RATIO $(A/F)_{in}$
STOICHIOMETRIC
AIR-FUEL RATIO
RICH

Fig.5

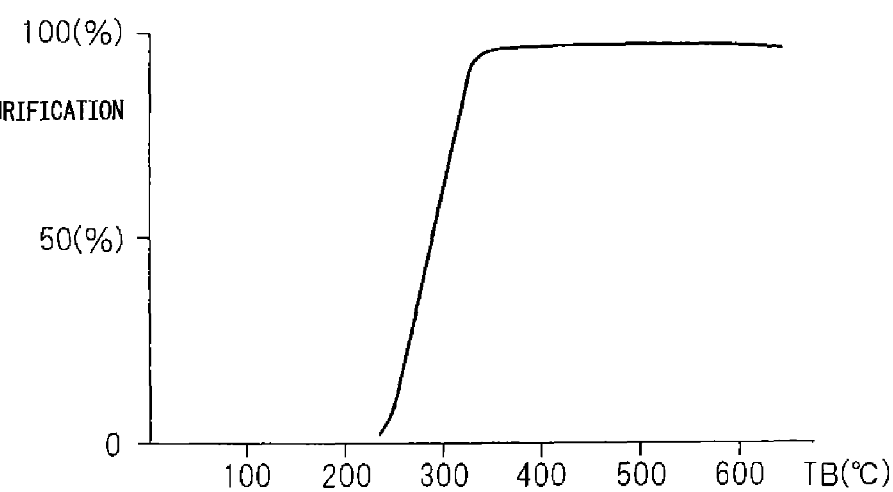

100(%)
NO_x PURIFICATION
RATE
50(%)
0
100
200
300
400
500
600
TB(℃)

Fig. 6A

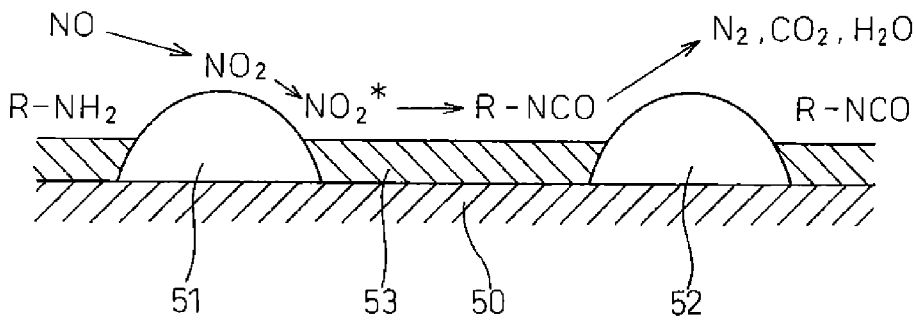

NO
NO2
NO2*
R-NCO
N2, CO2, H2O
R-NH2
R-NCO
51
53
50
52

Fig. 6B

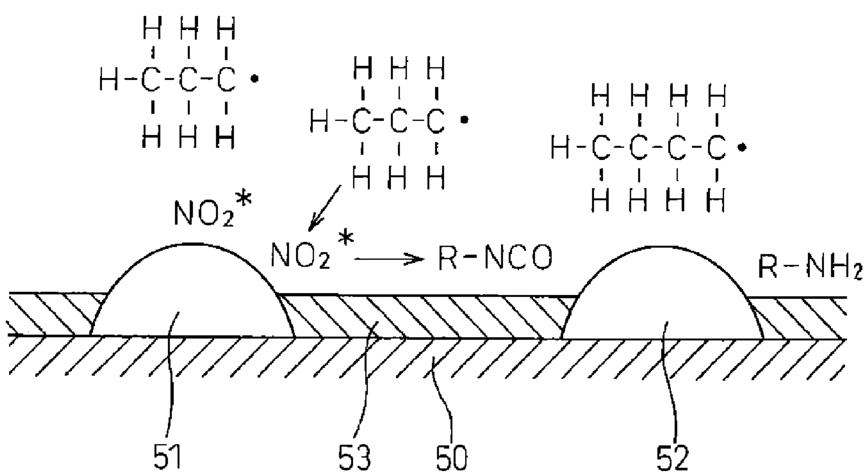

NO2*
NO2*
R-NCO
R-NH2
51
53
50
52

Fig. 7A

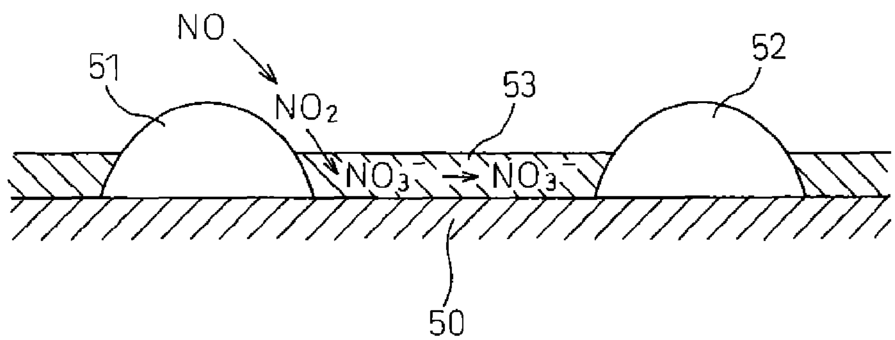


Fig. 7B

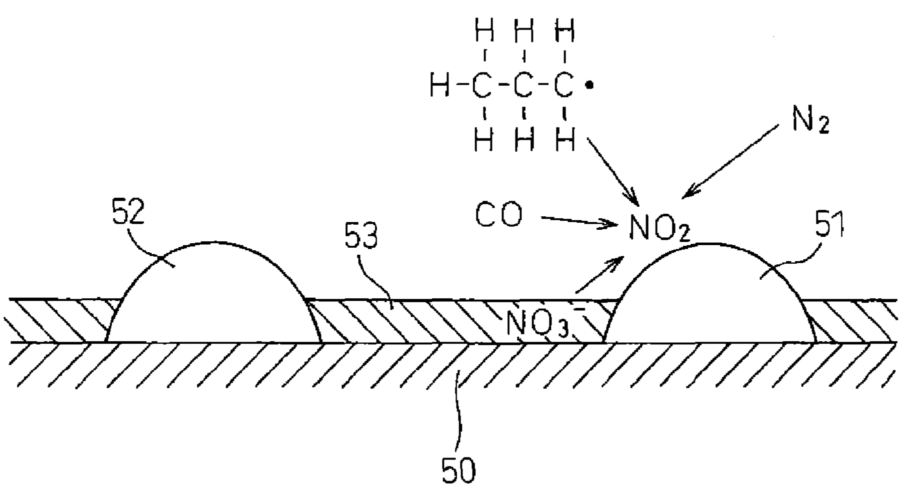


Fig.8

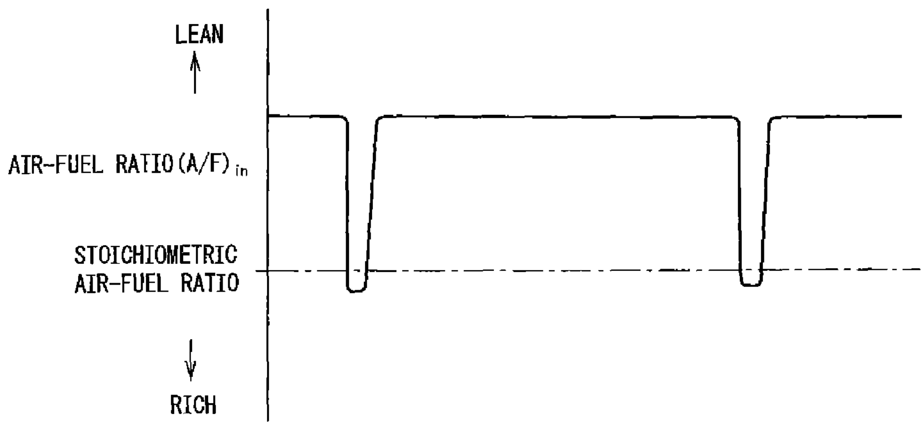

LEAN
AIR-FUEL RATIO $(A/F)_{in}$
STOICHIOMETRIC AIR-FUEL RATIO
RICH

Fig.9

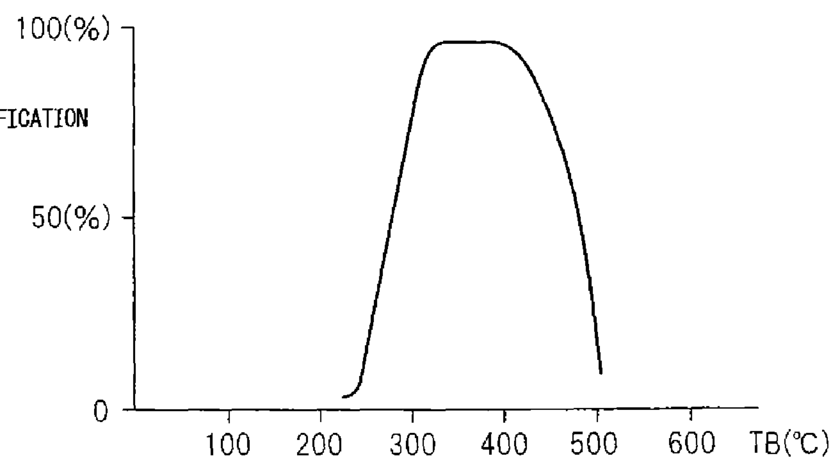

100(%)
NO_x PURIFICATION RATE
50(%)
0
100
200
300
400
500
600
TB(℃)

Fig.10

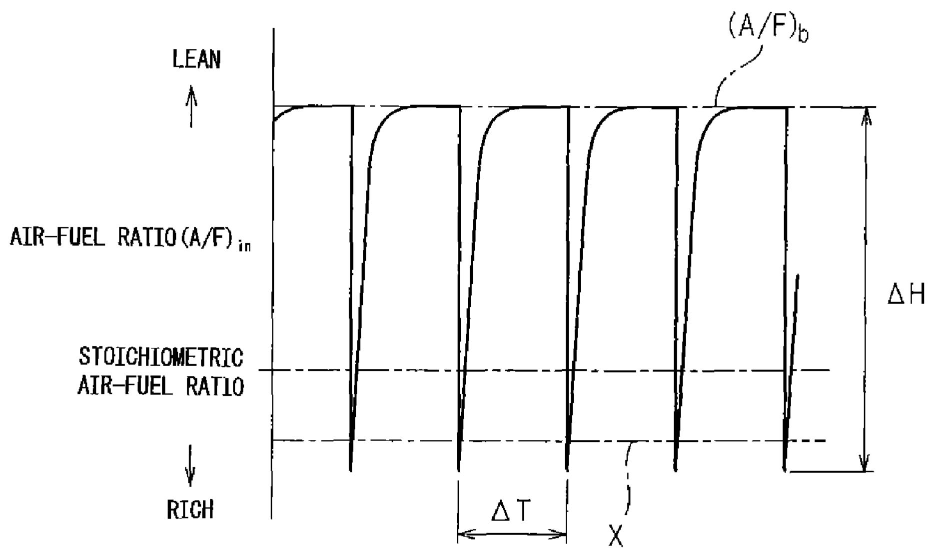

(A/F)b
LEAN
AIR-FUEL RATIO (A/F)in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
ΔH
ΔT
X

Fig.11

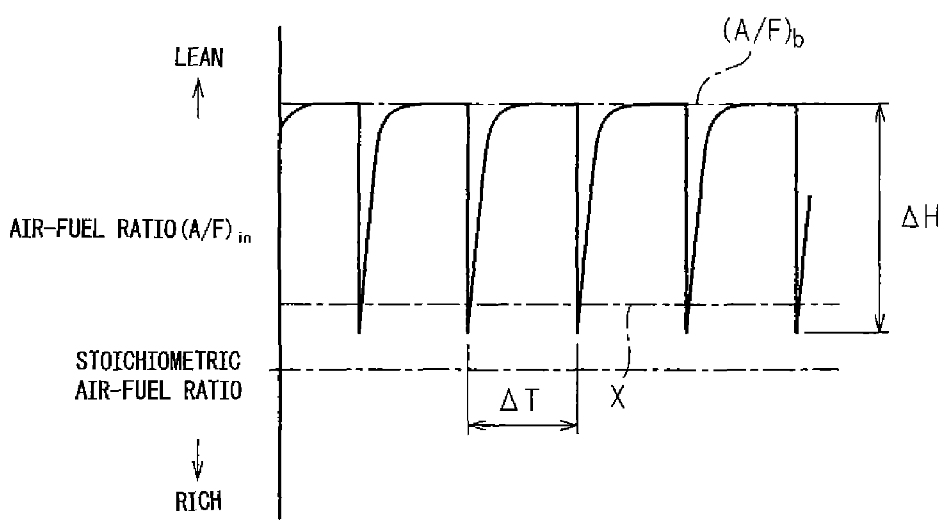

(A/F)b
LEAN
AIR-FUEL RATIO (A/F)in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
ΔH
ΔT
X

Fig. 12

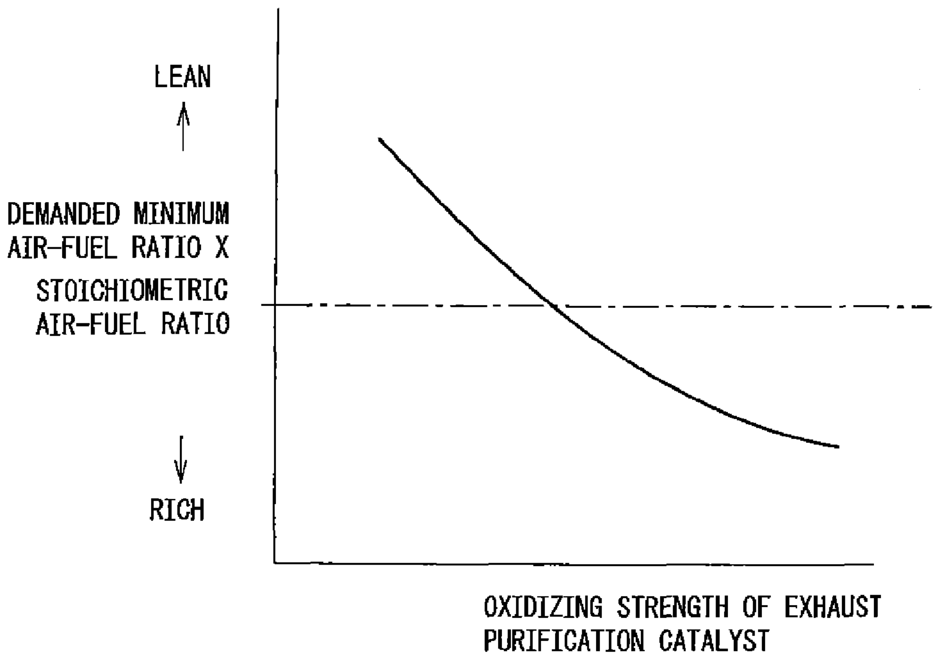

LEAN
DEMANDED MINIMUM AIR-FUEL RATIO X
STOICHIOMETRIC AIR-FUEL RATIO
RICH
OXIDIZING STRENGTH OF EXHAUST PURIFICATION CATALYST

Fig. 13

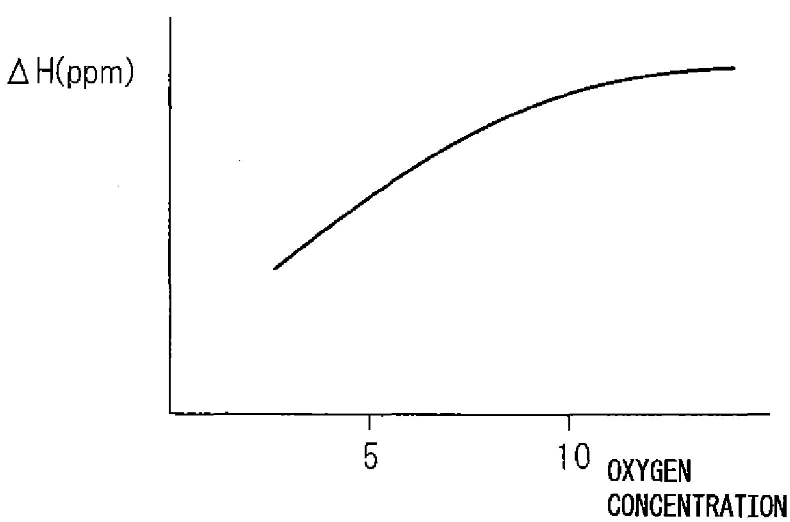
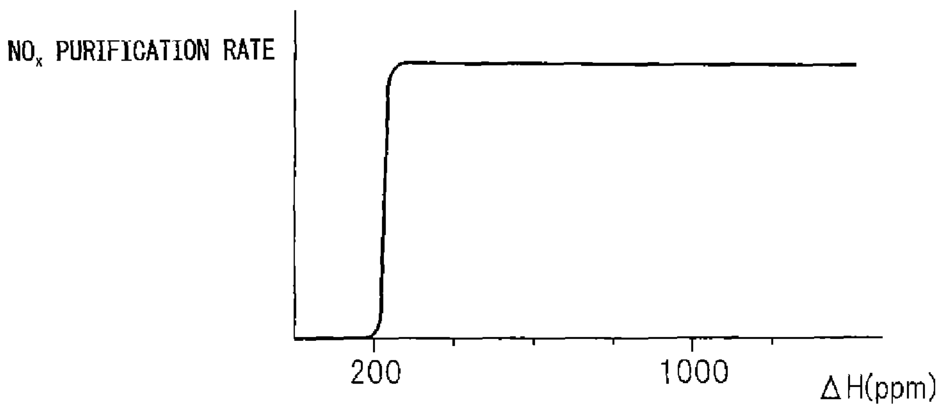
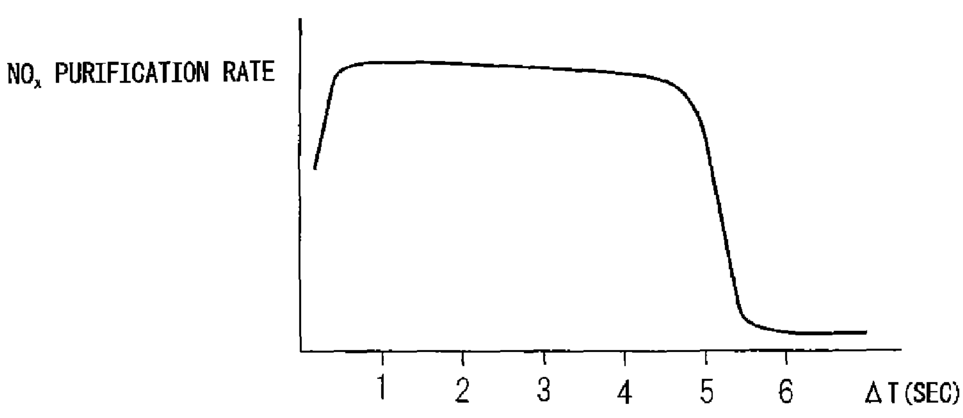

ΔH(ppm)
5
10
OXYGEN CONCENTRATION

Fig.14



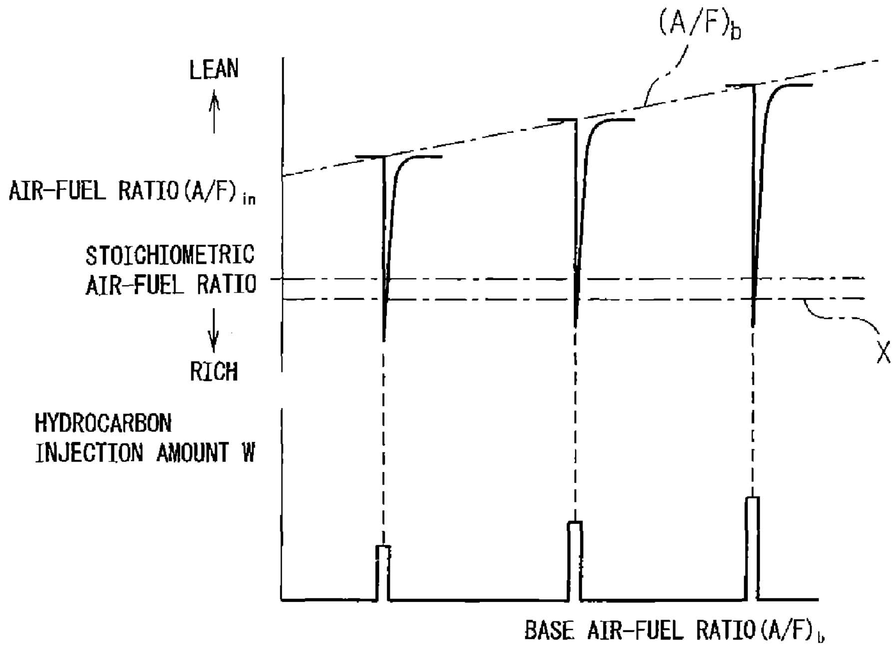
NO_x PURIFICATION RATE
200
1000
ΔH(ppm)

Fig.15



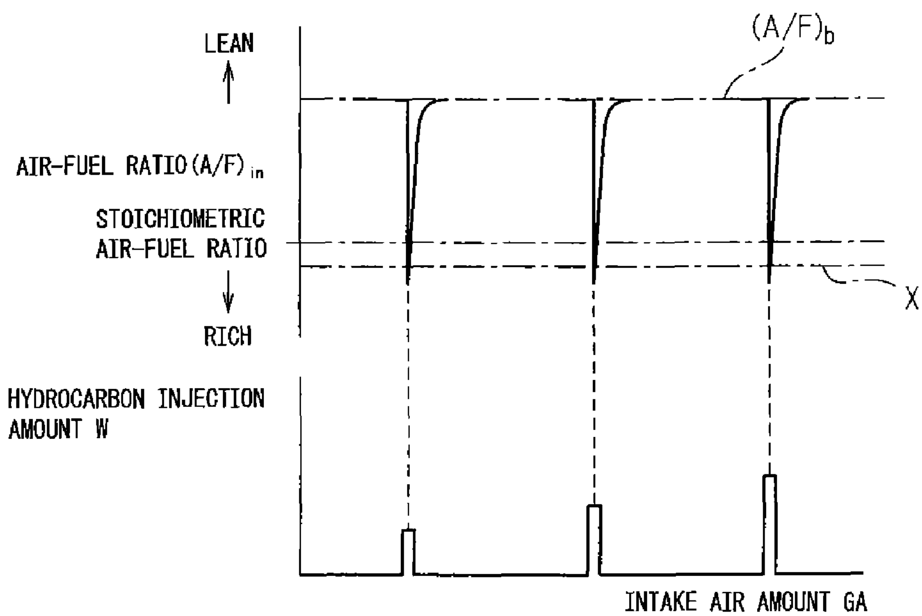
NO_x PURIFICATION RATE
1
2
3
4
5
6
ΔT(SEC)

Fig. 16



(A/F)b
LEAN
AIR-FUEL RATIO (A/F)in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
X
HYDROCARBON INJECTION AMOUNT W
BASE AIR-FUEL RATIO (A/F)b

Fig. 17



(A/F)b
LEAN
AIR-FUEL RATIO (A/F)in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
X
HYDROCARBON INJECTION AMOUNT W
INTAKE AIR AMOUNT GA

Fig.18

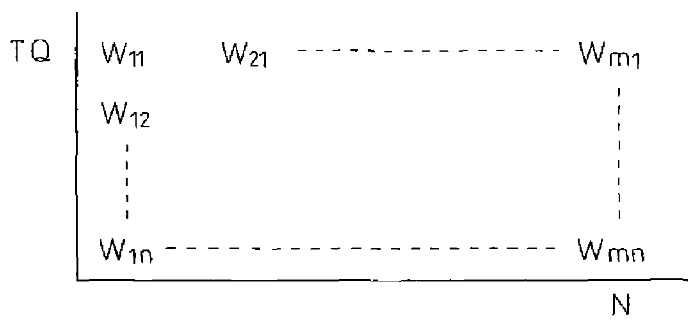

TQ
W11
W21
Wm1
W12
W1n
Wmn
N

Fig.19

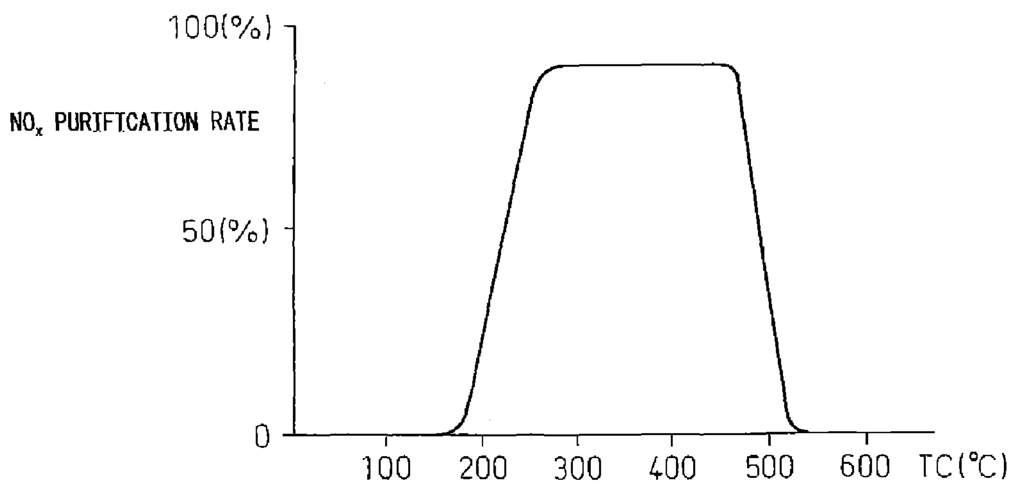

100(%)
NOx PURIFICATION RATE
50(%)
0
100
200
300
400
500
600
TC(°C)

Fig.20A

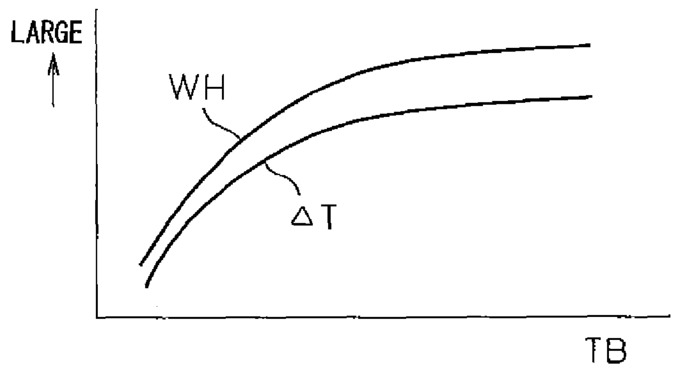


Fig.20B

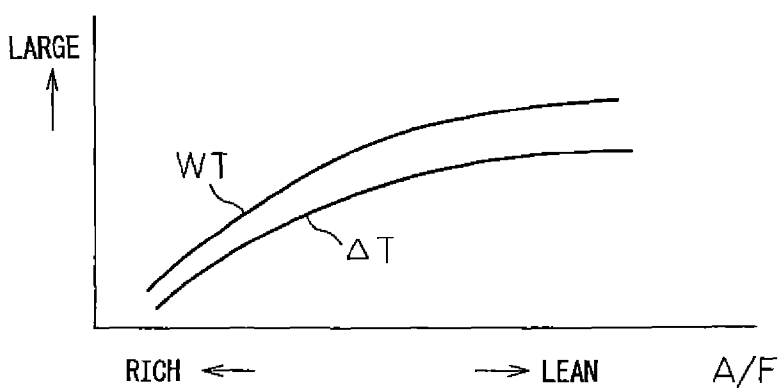


Fig.21A

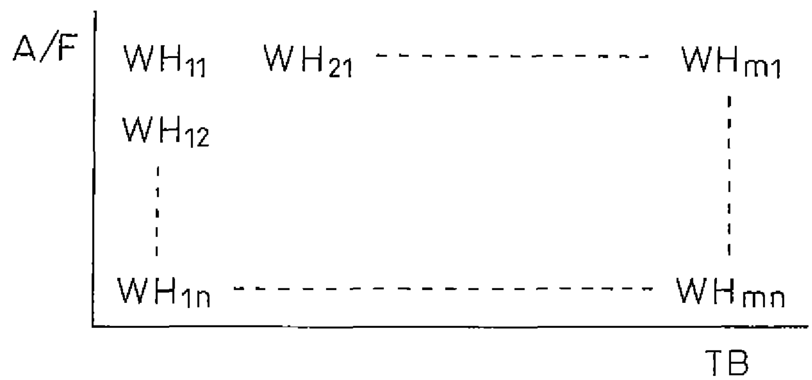


Fig.21B

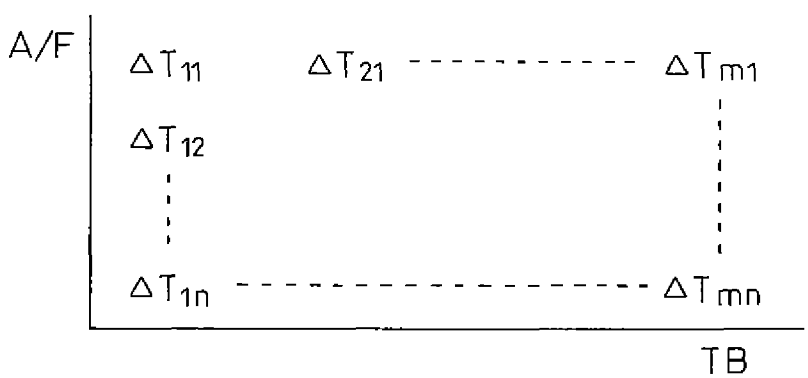


Fig.22

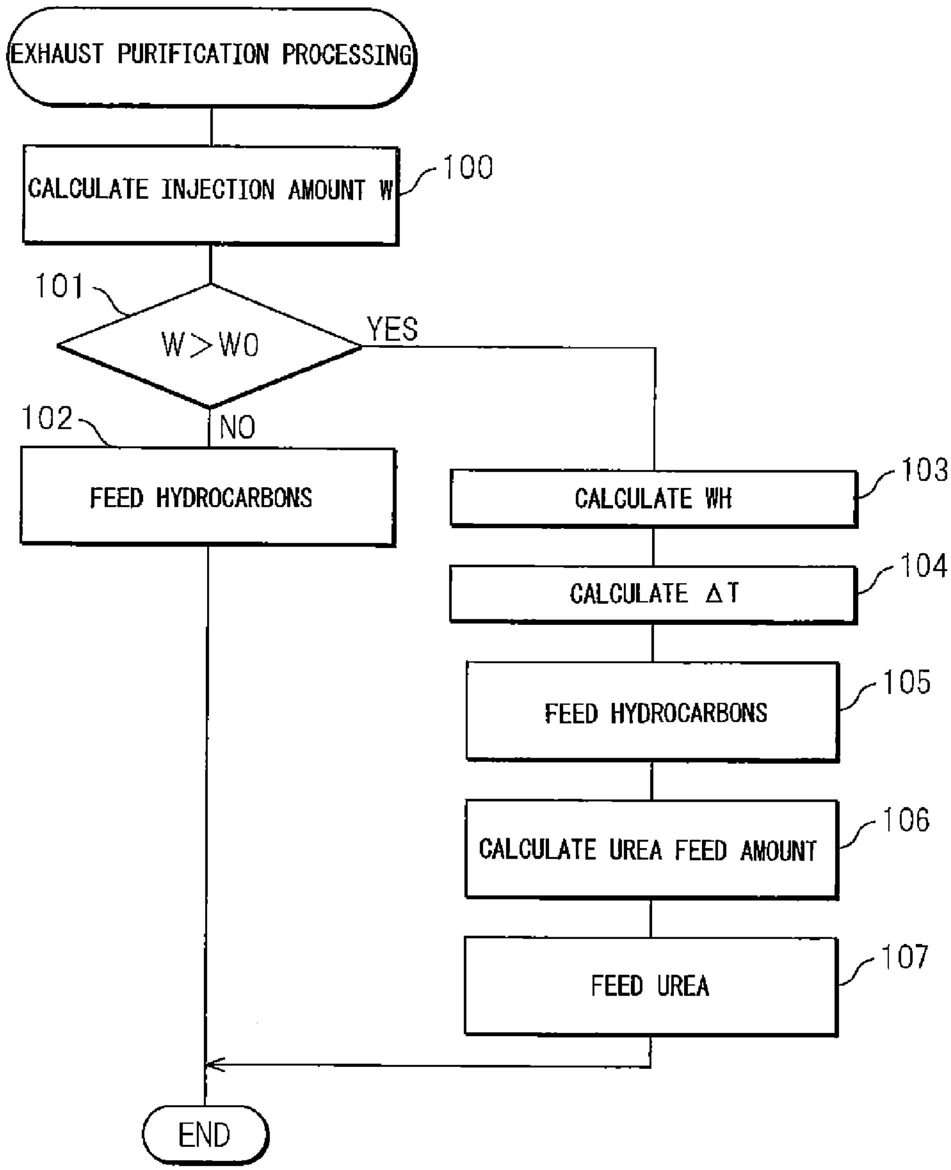

EXHAUST PURIFICATION PROCESSING
CALCULATE INJECTION AMOUNT W
100
101
W>W0
YES
NO
102
FEED HYDROCARBONS
CALCULATE WH
103
CALCULATE ΔT
104
FEED HYDROCARBONS
105
CALCULATE UREA FEED AMOUNT
106
FEED UREA
107
END

Fig.23

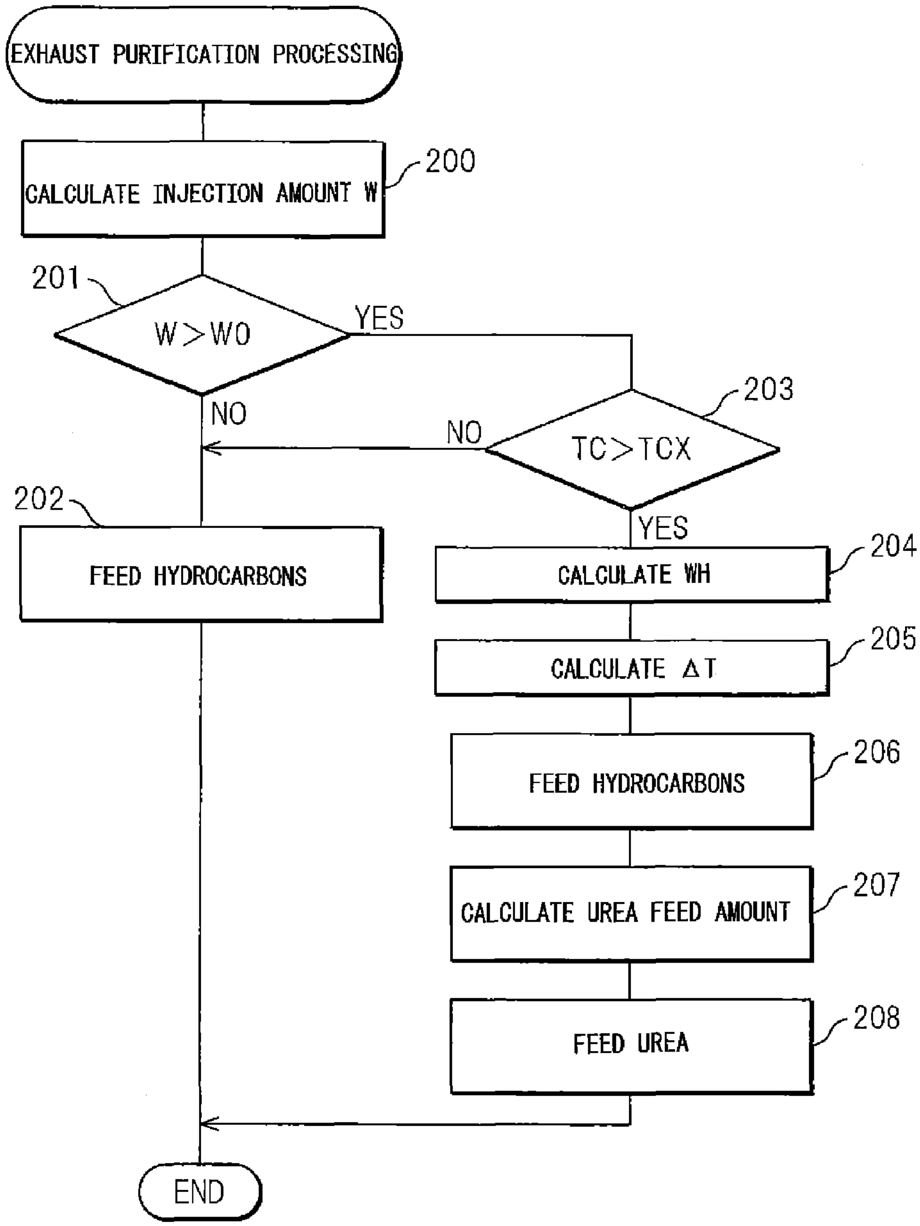

EXHAUST PURIFICATION PROCESSING
CALCULATE INJECTION AMOUNT W
200
201
W>W0
YES
NO
203
NO
TC>TCX
YES
202
FEED HYDROCARBONS
CALCULATE WH
204
CALCULATE ΔT
205
FEED HYDROCARBONS
206
CALCULATE UREA FEED AMOUNT
207
FEED UREA
208
END

Fig. 24

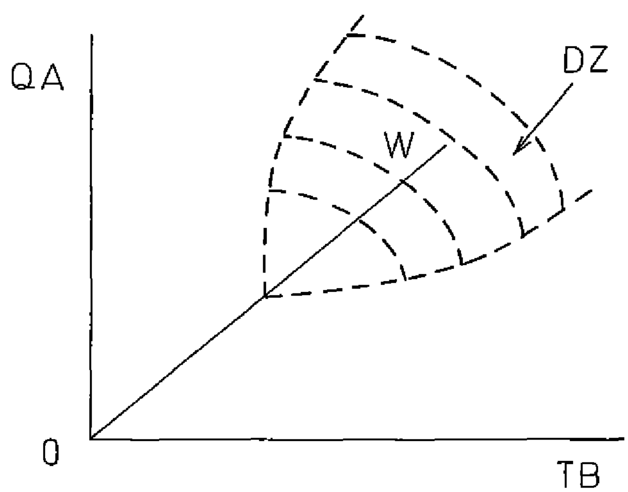
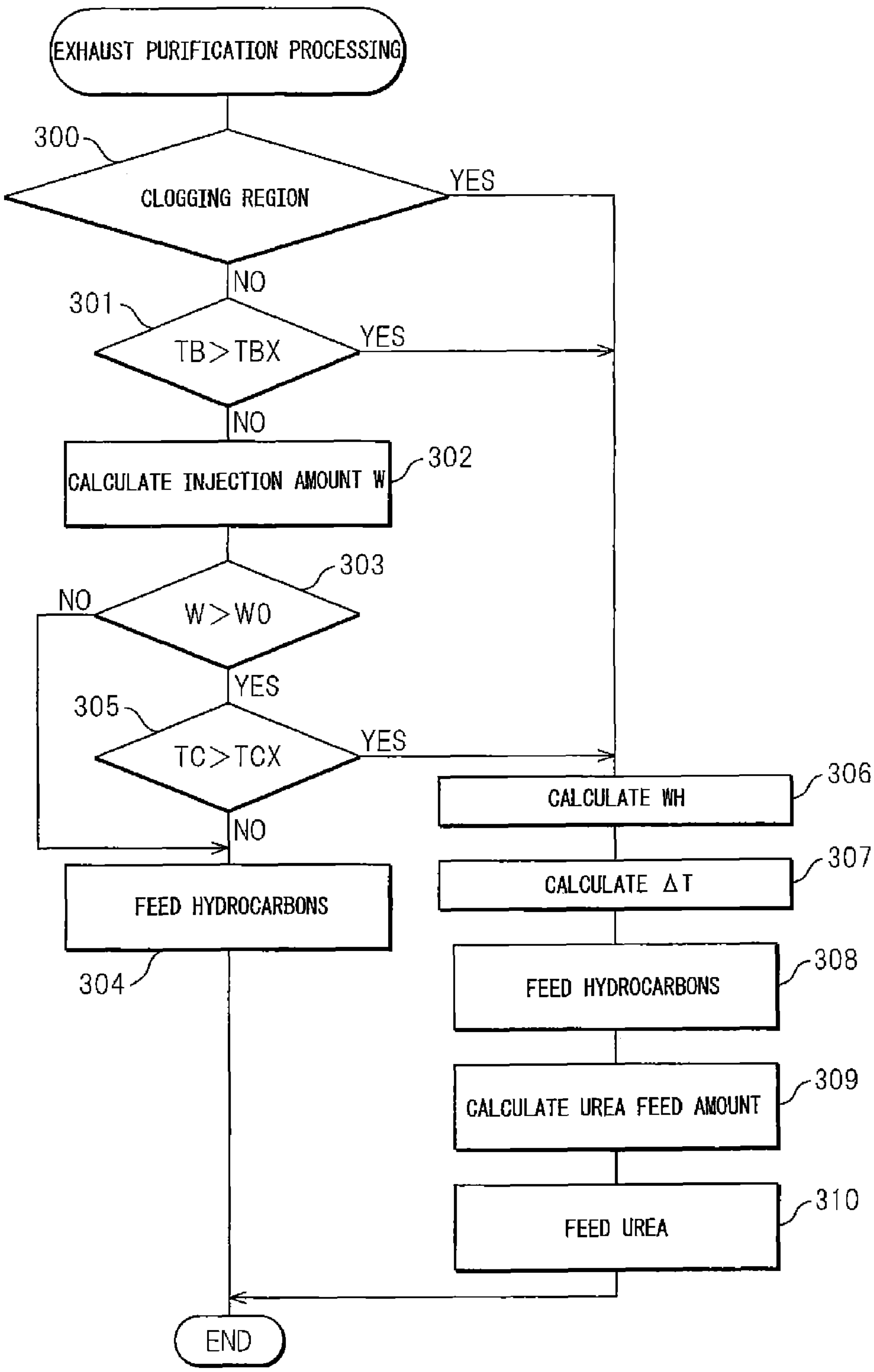


Fig.25


EXHAUST PURIFICATION PROCESSING
300
CLOGGING REGION
YES
NO
301
TB>TBX
YES
NO
CALCULATE INJECTION AMOUNT W
302
303
NO
W>W0
YES
305
TC>TCX
YES
NO
CALCULATE WH
306
CALCULATE ΔT
307
FEED HYDROCARBONS
304
FEED HYDROCARBONS
308
CALCULATE UREA FEED AMOUNT
309
FEED UREA
310
END

EXHAUST PURIFICATION SYSTEM OF INTERNAL COMBUSTION ENGINE

TECHNICAL FIELD

The present invention relates to an exhaust purification system of an internal combustion engine.

BACKGROUND ART

Known in the art is an internal combustion engine which arranges, in an engine exhaust passage, an NO_x storage catalyst which stores NO_x which is contained in exhaust gas when the air-fuel ratio of the inflowing exhaust gas is lean and which releases the stored NO_x when the air-fuel ratio of the inflowing exhaust gas becomes rich, which arranges, in the engine exhaust passage upstream of the NO_x storage catalyst, an oxidation catalyst which has an adsorption function, and which feeds hydrocarbons into the engine exhaust passage upstream of the oxidation catalyst to make the air-fuel ratio of the exhaust gas flowing into the NO_x storage catalyst rich when releasing NO_x from the NO_x storage catalyst (for example, see Patent Literature 1).

In this internal combustion engine, the hydrocarbons which are fed when releasing NO_x from the NO_x storage catalyst are made gaseous hydrocarbons at the oxidation catalyst, and the gaseous hydrocarbons are fed to the NO_x storage catalyst. As a result, the NO_x which is released from the NO_x storage catalyst is reduced well.

CITATION LIST

Patent Literature

Patent Literature 1: Japanese Patent No. 3969450

SUMMARY OF INVENTION

Technical Problem

However, there is the problem that when the NO_x storage catalyst becomes a high temperature, the NO_x purification rate falls.

An object of the present invention is to provide an exhaust purification system of an internal combustion engine which can give a high NO_x purification rate even if the temperature of the exhaust purification catalyst is a high temperature and which can reduce the amount of consumption of hydrocarbons.

Solution to Problem

According to the present invention, there is provided an exhaust purification system of an internal combustion engine wherein an exhaust purification catalyst for reacting NO_x contained in exhaust gas and reformed hydrocarbons is arranged inside of an engine exhaust passage, urea feeding means and an NO_x selective reduction catalyst able to reduce NO_x using ammonia derived from a fed urea are arranged inside of the engine exhaust passage downstream of the exhaust purification catalyst, a precious metal catalyst is carried on an exhaust gas flow surface of the exhaust purification catalyst and a basic exhaust gas flow surface part is formed around the precious metal catalyst, the exhaust purification catalyst has a property of reducing the NO_x which is contained in exhaust gas if making a concentration of hydrocarbons flowing into the exhaust purification catalyst vibrate by within a predetermined range of amplitude and within a predetermined range of period and has a property of being increased in storage amount of NO_x which is contained in exhaust gas when the vibration period of the hydrocarbon concentration is made longer than the predetermined range, and, at the time of engine operation, usually a first NO_x purification method which makes the concentration of hydrocarbons flowing into the exhaust purification catalyst vibrate by within the predetermined range of amplitude and within the predetermined range of period so as to reduce NO_x contained in exhaust gas in the exhaust purification catalyst is used, and a second NO_x purification method which uses an ammonia derived from the fed urea to reduce NO_x contained in exhaust gas at the NO_x selective reduction catalyst when a representative value representing an amount of hydrocarbons which is consumed for removal of NO_x using the first NO_x purification method exceeds a predetermined allowable value regardless of whether the NO_x selective reduction catalyst is activated or if the NO_x selective reduction catalyst is activated.

Advantageous Effects of Invention

Even if the temperature of the exhaust purification catalyst becomes a high temperature, a high NO_x purification rate can be obtained. Further, when a representative value exceeds the allowable value, that is, when the amount of consumption of hydrocarbons is increased, if the second NO_x purification method is used, the amount of consumption of hydrocarbons can be reduced.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is an overall view of a compression ignition type internal combustion engine.

FIG. **2** is a view schematically showing a surface part of a catalyst carrier.

FIG. **3** is a view for explaining an oxidation reaction in an exhaust purification catalyst.

FIG. **4** is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **5** is a view showing an NO_x purification rate.

FIGS. **6**A and **6**B are views for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIGS. **7**A and **7**B are views for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIG. **8** is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **9** is a view of an NO_x purification rate.

FIG. **10** is a time chart showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **11** is a time chart showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **12** is a view showing a relationship between an oxidizing strength of an exhaust purification catalyst and a demanded minimum air-fuel ratio X.

FIG. **13** is a view showing a relationship between an oxygen concentration in exhaust gas and an amplitude ΔH of a hydrocarbon concentration giving the same NO_x purification rate.

FIG. **14** is a view showing a relationship between an amplitude ΔH of a hydrocarbon concentration and an NO_x purification rate.

FIG. **15** is a view showing a relationship of a vibration period ΔT of a hydrocarbon concentration and an NO_x purification rate.

FIG. **16** is a time chart showing changes in an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst etc.

FIG. **17** is a time chart showing the changes in the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst etc.

FIG. **18** is a view showing a map of the hydrogen feed amount W.

FIG. **19** is a view showing an NO_x purification rate.

FIG. **20**A and FIG. **20**B are views showing the injection amount WH of hydrocarbons and injection interval ΔT.

FIG. **21**A and FIG. **21**B are views showing maps of the injection amount WH and injection interval ΔT.

FIG. **22** is a flow chart for exhaust purification control.

FIG. **23** is a flow chart for exhaust purification control.

FIG. **24** is a view showing a region where there is a danger of clogging occurring.

FIG. **25** is a flow chart for exhaust purification control.

DESCRIPTION OF EMBODIMENTS

FIG. **1** is an overall view of a compression ignition type internal combustion engine.

Referring to FIG. **1**, **1** indicates an engine body, **2** a combustion chamber of each cylinder, **3** an electronically controlled fuel injector for injecting fuel into each combustion chamber **2**, **4** an intake manifold, and **5** an exhaust manifold. The intake manifold **4** is connected through an intake duct **6** to an outlet of a compressor **7***a* of an exhaust turbocharger **7**, while an inlet of the compressor **7***a* is connected through an intake air amount detector **8** to an air cleaner **9**. Inside the intake duct **6**, a throttle valve **10** driven by a step motor is arranged. Furthermore, around the intake duct **6**, a cooling device **11** is arranged for cooling the intake air which flows through the inside of the intake duct **6**. In the embodiment shown in FIG. **1**, the engine cooling water is guided to the inside of the cooling device **11** where the engine cooling water is used to cool the intake air.

On the other hand, the exhaust manifold **5** is connected to an inlet of the exhaust turbine **7***b* of the exhaust turbocharger **7**. The outlet of the exhaust turbine **7***b* is connected through an exhaust pipe **12** to an inlet of an exhaust purification catalyst **13**, while an outlet of the exhaust purification catalyst **13** is connected to an NO_x selective reduction catalyst **15** which can reduce the NO_x which is contained in exhaust gas in the presence of ammonia through an exhaust pipe **14**. Inside of the exhaust pipe **12** upstream of the exhaust purification catalyst **13**, a hydrocarbon feed valve **16** is arranged for feeding hydrocarbons comprised of diesel oil or other fuel used as fuel of a compression ignition type internal combustion engine. In the embodiment shown in FIG. **1**, diesel oil is used as the hydrocarbons which are fed from the hydrocarbon feed valve **16**. Note that, the present invention can also be applied to a spark ignition type internal combustion engine which burns fuel under a lean air-fuel ratio. In this case, hydrocarbons comprised of gasoline or other fuel which is used as fuel of a spark ignition type internal combustion engine are fed from the hydrocarbon feed valve **16**.

In the exhaust pipe **14** upstream of the NO_x selective reduction catalyst **15**, an aqueous urea solution feed device, for example, an aqueous urea solution feed valve **17**, is arranged. This aqueous urea solution feed valve **17** is connected through a feed pipe **18** and a feed pump **19** to an aqueous urea solution tank **20**. The aqueous urea solution which is stored in the aqueous urea solution tank **20** is injected by the feed pump **19** into the exhaust gas which flows from the aqueous urea solution feed valve **17** to the inside of the exhaust pipe **14**. Due to the ammonia generated from the urea ($(NH_2)_2CO+H_2O \rightarrow 2NH_3+CO_2$), the NO_x which is contained in exhaust gas is reduced in the NO_x selective reduction catalyst **15**. In this embodiment shown in FIG. **1**, this NO_x selective reduction catalyst **15** is comprised of Fe zeolite.

On the other hand, the exhaust manifold **5** and the intake manifold **4** are connected with each other through an exhaust gas recirculation (hereinafter referred to as an "EGR") passage **21**. Inside the EGR passage **21**, an electronically controlled EGR control valve **22** is arranged. Further, around the EGR passage **21**, a cooling device **23** is arranged for cooling EGR gas flowing through the inside of the EGR passage **21**. In the embodiment shown in FIG. **1**, the engine cooling water is guided to the inside of the cooling device **23** where the engine cooling water is used to cool the EGR gas. On the other hand, each fuel injector **3** is connected through a fuel feed tube **24** to a common rail **24***a*. This common rail **24***a* is connected through an electronically controlled variable discharge fuel pump **25** to a fuel tank **26**. The fuel which is stored inside of the fuel tank **26** is fed by the fuel pump **25** to the inside of the common rail **24***a*. The fuel which is fed to the inside of the common rail **24***a* is fed through each fuel feed tube **24** to the fuel injector **3**.

An electronic control unit **30** is comprised of a digital computer provided with a ROM (read only memory) **32**, a RAM (random access memory) **33**, a CPU (microprocessor) **34**, an input port **35**, and an output port **36**, which are connected with each other by a bidirectional bus **31**. At the exhaust purification catalyst **13**, a temperature sensor **27** is attached for detecting the temperature of the exhaust purification catalyst **13**, while at the NO_x selective reduction catalyst **15**, a temperature sensor **28** is attached for detecting the temperature of the NO_x selective reduction catalyst **15**. Further, at the collecting portion of the exhaust manifold **5**, an air-fuel ratio sensor **29** is arranged. The output signals of these temperature sensors **27** and **28**, the air-fuel ratio sensor **29**, and the intake air amount detector **8** are input through respectively corresponding AD converters **37** to the input port **35**. Further, an accelerator pedal **40** has a load sensor **41** connected to it which generates an output voltage proportional to the amount of depression L of the accelerator pedal **40**. The output voltage of the load sensor **41** is input through a corresponding AD converter **37** to the input port **35**. Furthermore, at the input port **35**, a crank angle sensor **42** is connected which generates an output pulse every time a crankshaft rotates by, for example, 15°. On the other hand, the output port **36** is connected through corresponding drive circuits **38** to each fuel injector **3**, a step motor for driving the throttle valve **10**, hydrocarbon feed valve **16**, aqueous urea solution feed valve **17**, feed pump **18**, EGR control valve **22** and fuel pump **25**.

FIG. **2** schematically shows a surface part of a catalyst carrier which is carried on a substrate of the exhaust purification catalyst **13**. At this exhaust purification catalyst **13**, as shown in FIG. **2**, for example, there is provided a catalyst carrier **50** made of alumina on which precious metal catalysts **51** and **52** are carried. Furthermore, on this catalyst carrier **50**, a basic layer **53** is formed which includes at least one element selected from potassium K, sodium Na, cesium Cs, or another such alkali metal, barium Ba, calcium Ca, or another such alkali earth metal, a lanthanoid or another such rare earth and silver Ag, copper Cu, iron Fe, iridium Ir, or another metal able to donate electrons to NO_x. The exhaust gas flows along the top of the catalyst carrier **50**, so the precious metal catalysts **51** and **52** can be said to be carried on the exhaust gas flow surface of the exhaust purification catalyst **13**. Further, the surface of the basic layer **53** exhibits basicity, so the surface of the basic layer **53** is called the basic exhaust gas flow surface part **54**.

On the other hand, in FIG. **2**, the precious metal catalyst **51** is comprised of platinum Pt, while the precious metal catalyst **52** is comprised of rhodium Rh. That is, the precious metal catalysts **51** and **52** which are carried on the catalyst carrier **50** are comprised of platinum Pt and rhodium Rh. Note that, on the catalyst carrier **50** of the exhaust purification catalyst **13**, in addition to platinum Pt and rhodium Rh, palladium Pd may be further carried or, instead of rhodium Rh, palladium Pd may be carried. That is, the precious metal catalysts **51** and **52** which are carried on, the catalyst carrier **50** are comprised of platinum Pt and at least one of rhodium Rh and palladium Pd.

If hydrocarbons are injected from the hydrocarbon feed valve **16** into the exhaust gas, the hydrocarbons are reformed by the exhaust purification catalyst **13**. In the present invention, at this time, the reformed hydrocarbons are used to remove the NO_x at the exhaust purification catalyst **13**. FIG. **3** schematically shows the reforming action performed at the exhaust purification catalyst **13** at this time. As shown in FIG. **3**, the hydrocarbons HC which are injected from the hydrocarbon feed valve **16** become radical hydrocarbons HC with a small carbon number by the catalyst **51**.

Note that, even if injecting fuel, that is, hydrocarbons, from the fuel injector **3** into the combustion chamber **2** during the latter half of the expansion stroke or during the exhaust stroke, the hydrocarbons are reformed inside of the combustion chamber **2** or at the exhaust purification catalyst **13**, and the NO_x which is contained in the exhaust gas is removed by the reformed hydrocarbons at the exhaust purification catalyst **13**. Therefore, in the present invention, instead of feeding hydrocarbons from the hydrocarbon feed valve **16** to the inside of the engine exhaust passage, it is also possible to feed hydrocarbons into the combustion chamber **2** during the latter half of the expansion stroke or during the exhaust stroke. In this way, in the present invention, it is also possible to feed hydrocarbons to the inside of the combustion chamber **2**, but below the present invention is explained taking as an example the case of injecting hydrocarbons from the hydrocarbon feed valve **16** to the inside of the engine exhaust passage.

FIG. **4** shows the timing of feeding hydrocarbons from the hydrocarbon feed valve **16** and the changes in the air-fuel ratio (A/F)in of the exhaust gas flowing into the exhaust purification catalyst **13**. Note that, the changes in the air-fuel ratio (A/F)in depend on the change in concentration of the hydrocarbons in the exhaust gas which flows into the exhaust purification catalyst **13**, so it can be said that the change in the air-fuel ratio (A/F)in shown in FIG. **4** expresses the change in concentration of the hydrocarbons. However, if the hydrocarbon concentration becomes higher, the air-fuel ratio (A/F)in becomes smaller, so, in FIG. **4**, the more to the rich side the air-fuel ratio (A/F)in becomes, the higher the hydrocarbon concentration.

FIG. **5** shows the NO_x purification rate by the exhaust purification catalyst **13** with respect to the catalyst temperature TB of the exhaust purification catalyst **13** when periodically making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** change so as to, as shown in FIG. **4**, make the air-fuel ratio (A/F)in of the exhaust gas flowing to the exhaust purification catalyst **13** change. The inventors engaged in research relating to NO_x purification for a long time. In the process of research, they learned that if making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** vibrate by within a predetermined range of amplitude and within a predetermined range of period, as shown in FIG. **5**, an extremely high NO_x purification rate is obtained even in a 400° C. or higher high temperature region.

Furthermore, at this time, a large amount of reducing intermediate containing nitrogen and hydrocarbons continues to be held or adsorbed on the surface of the basic layer **53**, that is, on the basic exhaust gas flow surface part **54** of the exhaust purification catalyst **13**. It is learned that this reducing intermediate plays a central role in obtaining a high NO_x purification rate. Next, this will be explained with reference to FIGS. **6**A and **6**B. Note that, these FIGS. **6**A and **6**B schematically show the surface part of the catalyst carrier **50** of the exhaust purification catalyst **13**. These FIGS. **6**A and **6**B show the reaction which is presumed to occur when the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is made to vibrate by within a predetermined range of amplitude and within a predetermined range of period.

FIG. **6**A shows when the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is low, while FIG. **6**B shows when hydrocarbons are fed from the hydrocarbon feed valve **16** and the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** becomes high.

Now, as will be understood from FIG. **4**, the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **13** is maintained lean except for an instant, so the exhaust gas which flows into the exhaust purification catalyst **13** normally becomes a state of oxygen excess. Therefore, the NO which is contained in the exhaust gas, as shown in FIG. **6**A, is oxidized on the platinum **51** and becomes NO_2. Next, this NO_2 is supplied with electrons from the platinum **51** and becomes NO_2^-. Therefore, a large amount of NO_2^- is produced on the platinum **51**. This NO_2^- is strong in activity. Above, this NO_2^- is called the active NO_2^*.

On the other hand, if hydrocarbons are fed from the hydrocarbon feed valve **15**, as shown in FIG. **3**, the hydrocarbons are reformed and become radicalized inside of the exhaust purification catalyst **13**. As a result, as shown in FIG. **6**B, the hydrocarbon concentration around the active NO_2^* becomes higher. In this regard, after the active NO_2^* is produced, if the state of a high oxygen concentration around the active NO_2^* continues for a predetermined time or more, the active NO_2^* is oxidized and is absorbed in the basic layer **53** in the form of nitrate ions NO_3^-. However, if the hydrocarbon concentration around the active NO_2 is made higher before this predetermined time passes, as shown in FIG. **6**B, the active NO_2^* reacts on the platinum **51** with the radical hydrocarbons HC whereby a reducing intermediate is produced. This reducing intermediate is adhered or adsorbed on the surface of the basic layer **53**.

Note that, at this time, the first produced reducing intermediate is considered to be a nitro compound $R—NO_2$. If this nitro compound $R—NO_2$ is produced, the result becomes a nitrile compound R—CN, but this nitrile compound R—CN can only survive for an instant in this state, so immediately becomes an isocyanate compound R—NCO. This isocyanate compound R—NCO, when hydrolyzed, becomes an amine compound $R—NH_2$. However, in this case, what is hydrolyzed is considered to be part of the isocyanate compound R—NCO. Therefore, as shown in FIG. **6**B, the majority of the reducing intermediate which is held or adsorbed on the surface of the basic layer **53** is believed to be the isocyanate compound R—NCO and amine compound $R—NH_2$.

On the other hand, as shown in FIG. **6**B, if the produced reducing intermediate is surrounded by the hydrocarbons HC, the reducing intermediate is blocked by the hydrocarbons HC and the reaction will not proceed any further. In this case, if the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is lowered and thereby the oxygen concentration becomes higher, the hydrocarbons around the reducing intermediate will be oxidized. As a result, as shown in FIG. **6**A, the reducing intermediate and the active NO_2* will react. At this time, the active NO_2^* reacts with the reducing intermediate R—NCO or R—NH_2 to form N_2, CO_2, and H_2O and consequently the NO_x is removed.

In this way, in the exhaust purification catalyst **13**, by making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** higher, a reducing intermediate is produced. By making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** lower and raising the oxygen concentration, the active NO_2* reacts with the reducing intermediate and the NO_x is removed. That is, in order for the exhaust purification catalyst **13** to remove the NO_x, the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** has to be periodically changed.

Of course, in this case, it is necessary to raise the concentration of hydrocarbons to a concentration sufficiently high for producing the reducing intermediate and it is necessary to lower the concentration of hydrocarbons to a concentration sufficiently low for making the produced reducing intermediate react with the active NO_2*. That is, the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** has to be made to vibrate within a predetermined range of amplitude. Note that, in this case, a sufficient amount of reducing intermediate R—NCO or R—NH_2 has to be held on the basic layer **53**, that is, on the basic exhaust gas flow surface part **54**, until the produced reducing intermediate reacts with the active NO_2*. For this reason, the basic exhaust gas flow surface part **54** is provided.

On the other hand, if lengthening the feed period of the hydrocarbons, the time in which the oxygen concentration becomes higher becomes longer in the period after the hydrocarbons are fed until the hydrocarbons are next fed. Therefore, the active NO_2* is absorbed in the basic layer **53** in the form of nitrates without producing a reducing intermediate. To avoid this, it is necessary to make the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** vibrate by within a predetermined range of period.

Therefore, in an embodiment of the present invention, to make the NO_x contained in the exhaust gas and the reformed hydrocarbons react and produce the reducing intermediate R—NCO or R—NH_2 containing nitrogen and hydrocarbons, precious metal catalysts **51** and **52** are carried on the exhaust gas flow surface of the exhaust purification catalyst **13**. To hold the produced reducing intermediate R—NCO or R—NH_2 inside the exhaust purification catalyst **13**, a basic exhaust gas flow surface part **54** is formed around the precious metal catalysts **51** and **52**. NO_x is reduced by the reducing action of the reducing intermediate R—NCO or R—NH_2 held on the basic exhaust gas flow surface part **54**, and the vibration period of the hydrocarbon concentration is made the vibration period required for continuation of the production of the reducing intermediate R—NCO or R—NH_2. Incidentally, in the example shown in FIG. **4**, the injection interval is made 3 seconds.

If the vibration period of the hydrocarbon concentration, that is, the feed period of the hydrocarbons HC, is made longer than the above predetermined range of period, the reducing intermediate R—NCO or R—NH_2 disappears from the surface of the basic layer **53**. At this time, the active NO_2* which is produced on the platinum Pt **51**, as shown in FIG. **7**A, diffuses in the basic layer **53** in the form of nitrate ions NO_3^- and becomes nitrates. That is, at this time, the NO_x in the exhaust gas is absorbed in the form of nitrates inside of the basic layer **53**.

On the other hand, FIG. **7**B shows the case where the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **13** is made the stoichiometric air-fuel ratio or rich when the NO_x is absorbed in the form of nitrates inside of the basic layer **53**. In this case, the oxygen concentration in the exhaust gas falls, so the reaction proceeds in the opposite direction ($NO_3^- \rightarrow NO_2$), and consequently the nitrates absorbed in the basic layer **53** become nitrate ions NO_3 one by one and, as shown in FIG. **7**B, are released from the basic layer **53** in the form of NO_2. Next, the released NO_2 is reduced by the hydrocarbons HC and CO contained in the exhaust gas.

FIG. **8** shows the case of making the air-fuel ratio (A/F)in of the exhaust gas which flows into the exhaust purification catalyst **13** temporarily rich slightly before the NO_x absorption ability of the basic layer **53** becomes saturated. Note that, in the example shown in FIG. **8**, the time interval of this rich control is 1 minute or more. In this case, the NO_x which was absorbed in the basic layer **53** when the air-fuel ratio (A/F)in of the exhaust gas was lean is released all at once from the basic layer **53** and reduced when the air-fuel ratio (A/F)in of the exhaust gas is made temporarily rich. Therefore, in this case, the basic layer **53** plays the role of an absorbent for temporarily absorbing NO_x.

Note that, at this time, sometimes the basic layer **53** temporarily adsorbs the NO_x. Therefore, if using term of storage as a term including both absorption and adsorption, at this time, the basic layer **53** performs the role of an NO_x storage agent for temporarily storing the NO_x. That is, in this case, if the ratio of the air and fuel (hydrocarbons) which are supplied into the engine intake passage, combustion chambers **2** and exhaust passage upstream of the exhaust purification catalyst **13** is referred to as the air-fuel ratio of the exhaust gas, the exhaust purification catalyst **13** functions as an NO_x storage catalyst which stores the NO_x when the air-fuel ratio of the exhaust gas is lean and releases the stored NO_x when the oxygen concentration in the exhaust gas falls.

FIG. **9** shows the NO_x purification rate when making the exhaust purification catalyst **13** function as an NO_x storage catalyst in this way. Note that, the abscissa of the FIG. **9** shows the catalyst temperature TC of the exhaust purification catalyst **13**. When making the exhaust purification catalyst **13** function as an NO_x storage catalyst, as shown in FIG. **9**, when the catalyst temperature TC is 300° C. to 400° C., an extremely high NO_x purification rate is obtained, but when the catalyst temperature TC becomes a 400° C. or higher high temperature, the NO_x purification rate falls.

In this way, when the catalyst temperature TC becomes 400° C. or more, the NO_x purification rate falls because if the catalyst temperature TC becomes 400° C. or more, the nitrates break down by heat and are released in the form of NO_2 from the exhaust purification catalyst **13**. That is, so long as storing NO_x in the form of nitrates, when the catalyst temperature TC is high, it is difficult to obtain a high NO_x purification rate. However, in the new NO_x purification method shown from FIG. **4** to FIGS. **6**A and **6**B, as will be understood from FIGS. **6**A and **6**B, nitrates are not formed or even if formed are extremely fine in amount, consequently, as shown in FIG. **5**, even when the catalyst temperature TC is high, a high NO_x purification rate is obtained.

Therefore, in the present invention, an exhaust purification catalyst **13** is arranged in the engine exhaust passage for reacting the NO_x which is contained in the exhaust gas and the reformed hydrocarbon. Precious metal catalysts **51** and **52** are carried on the exhaust gas flow surface of the exhaust purification catalyst **13**. Around the precious metal catalysts **51** and **52**, a basic exhaust gas flow surface part **54** is formed. The exhaust purification catalyst **13** has the property of reducing the NO_x which is contained in the exhaust gas if making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** vibrate by within a predetermined range of amplitude and within a predetermined range of period and has the property of being increased in storage amount of the NO_x which is contained in the exhaust gas if making the vibration period of the hydrocarbon concentration longer than this predetermined range. At the time of engine operation, usually, the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is made to vibrate within the predetermined range of amplitude and within the predetermined range of period. Due to this, the NO_x which is contained in the exhaust gas is reduced in the exhaust purification catalyst **13**.

That is, the NO_x purification method which is shown from FIG. **4** to FIGS. **6**A and **6**B can be said to be a new NO_x purification method designed to remove NO_x without forming almost any nitrates in the case of using an exhaust purification catalyst which carries a precious metal catalyst and forms a basic layer which can absorb NO_x. In actuality, when using this new NO_x purification method, the nitrates which are detected from the basic layer **53** become much smaller in amount compared with the case where making the exhaust purification catalyst **13** function as an NO_x storage catalyst. This new NO_x purification method will be called the first NO_x purification method below.

Next, referring to FIG. **10** to FIG. **15**, this first NO_x purification method will be explained in more detail.

FIG. **10** shows enlarged the change in the air-fuel ratio (A/F)in shown in FIG. **4**. Note that, as explained above, the change in the air-fuel ratio (A/F)in of the exhaust gas flowing into this exhaust purification catalyst **13** simultaneously shows the change in concentration of the hydrocarbons which flow into the exhaust purification catalyst **13**. Note that, in FIG. **10**, ΔH shows the amplitude of the change in concentration of hydrocarbons HC which flow into the exhaust purification catalyst **13**, while ΔT shows the vibration period of the concentration of the hydrocarbons which flow into the exhaust purification catalyst **13**.

Furthermore, in FIG. **10**, (A/F)b shows the base air-fuel ratio which shows the air-fuel ratio of the combustion gas for generating the engine output. In other words, this base air-fuel ratio (A/F)b shows the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **13** when stopping the feed of hydrocarbons. On the other hand, in FIG. **10**, X shows the upper limit of the air-fuel ratio (A/F)in which is used for producing the reducing intermediate without the produced active NO_2* being stored in the form of nitrates inside the basic layer **53**. To make the active NO_2* and the reformed hydrocarbons react and produce the reducing intermediate, it is necessary to make the air-fuel ratio (A/F)in lower than the upper limit X of this air-fuel ratio.

In other words, in FIG. **10**, X shows the lower limit of the concentration of hydrocarbons required for making the active NO_2* and reformed hydrocarbon react to produce a reducing intermediate. To produce the reducing intermediate, the concentration of hydrocarbons has to be made higher than this lower limit X. In this case, whether the reducing intermediate is produced is determined by the ratio of the oxygen concentration and hydrocarbon concentration around the active NO_2*, that is, the air-fuel ratio (A/F)in. The upper limit X of the air-fuel ratio required for producing the reducing intermediate will below be called the demanded minimum air-fuel ratio.

In the example shown in FIG. **10**, the demanded minimum air-fuel ratio X is rich, therefore, in this case, to form the reducing intermediate, the air-fuel ratio (A/F)in is instantaneously made the demanded minimum air-fuel ratio X or less, that is, rich. As opposed to this, in the example shown in FIG. **11**, the demanded minimum air-fuel ratio X is lean. In this case, the air-fuel ratio (A/F)in is maintained lean while periodically reducing the air-fuel ratio (A/F)in so as to form the reducing intermediate.

In this case, whether the demanded minimum air-fuel ratio X becomes rich or becomes lean depends on the oxidizing strength of the exhaust purification catalyst **13**. In this case, the exhaust purification catalyst **13**, for example, becomes stronger in oxidizing strength if increasing the carried amount of the precious metal **51** and becomes stronger in oxidizing strength if strengthening the acidity. Therefore, the oxidizing strength of the exhaust purification catalyst **13** changes due to the carried amount of the precious metal **51** or the strength of the acidity.

Now, if using an exhaust purification catalyst **13** with a strong oxidizing strength, as shown in FIG. **11**, if maintaining the air-fuel ratio (A/F)in lean while periodically lowering the air-fuel ratio (A/F)in, the hydrocarbons end up becoming completely oxidized when the air-fuel ratio (A/F)in is reduced. As a result, the reducing intermediate can no longer be produced. As opposed to this, when using an exhaust purification catalyst **13** with a strong oxidizing strength, as shown in FIG. **10**, if making the air-fuel ratio (A/F)in periodically rich, when the air-fuel ratio (A/F)in is made rich, the hydrocarbons will be partially oxidized, without being completely oxidized, that is, the hydrocarbons will be reformed, consequently the reducing intermediate will be produced. Therefore, when using an exhaust purification catalyst **13** with a strong oxidizing strength, the demanded minimum air-fuel ratio X has to be made rich.

On the other hand, when using an exhaust purification catalyst **13** with a weak oxidizing strength, as shown in FIG. **11**, if maintaining the air-fuel ratio (A/F)in lean while periodically lowering the air-fuel ratio (A/F)in, the hydrocarbons will be partially oxidized without being completely oxidized, that is, the hydrocarbons will be reformed and consequently the reducing intermediate will be produced. As opposed to this, when using an exhaust purification catalyst **13** with a weak oxidizing strength, as shown in FIG. **10**, if making the air-fuel ratio (A/F)in periodically rich, a large amount of hydrocarbons will be exhausted from the exhaust purification catalyst **13** without being oxidized and consequently the amount of hydrocarbons which is wastefully consumed will increase. Therefore, when using an exhaust purification catalyst **13** with a weak oxidizing strength, the demanded minimum air-fuel ratio X has to be made lean.

That is, it is learned that the demanded minimum air-fuel ratio X, as shown in FIG. **12**, has to be reduced the stronger the oxidizing strength of the exhaust purification catalyst **13**. In this way the demanded minimum air-fuel ratio X becomes lean or rich due to the oxidizing strength of the exhaust purification catalyst **13**. Below, taking as example the case where the demanded minimum air-fuel ratio X is rich, the amplitude of the change in concentration of hydrocarbons flowing into the exhaust purification catalyst **13** and the vibration period of the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** will be explained.

Now, if the base air-fuel ratio (A/F)b becomes larger, that is, if the oxygen concentration in the exhaust gas before the hydrocarbons are fed becomes higher, the feed amount of hydrocarbons required for making the air-fuel ratio (A/F)in the demanded minimum air-fuel ratio X or less increases and along with this the excess amount of hydrocarbons which did not contribute the production of the reducing intermediate also increases. In this case, to remove the NO_x well, as explained above, it is necessary to make the excess hydrocarbons oxidize. Therefore, to remove the NO_x well, the larger the amount of excess hydrocarbons, the larger the amount of oxygen which is required.

In this case, if raising the oxygen concentration in the exhaust gas, the amount of oxygen can be increased. Therefore, to remove the NO_x well, when the oxygen concentration in the exhaust gas before the hydrocarbons are fed is high, it is necessary to raise the oxygen concentration in the exhaust gas after feeding the hydrocarbons. That is, the higher the oxygen concentration in the exhaust gas before the hydrocarbons are fed, the larger the amplitude of the hydrocarbon concentration has to be made.

FIG. **13** shows the relationship between the oxygen concentration in the exhaust gas before the hydrocarbons are fed and the amplitude ΔH of the hydrocarbon concentration when the same NO_x purification rate is obtained. From FIG. **13**, it is learned that, to obtain the same NO_x purification rate, the higher the oxygen concentration in the exhaust gas before the hydrocarbons are fed, the greater the amplitude ΔH of the hydrocarbon concentration has to be made. That is, to obtain the same NO_x purification rate, the higher the base air-fuel ratio (A/F)b, the greater the amplitude ΔT of the hydrocarbon concentration has to be made. In other words, to remove the NO_x well, the lower the base air-fuel ratio (A/F)b, the more the amplitude ΔT of the hydrocarbon concentration can be reduced.

In this regard, the base air-fuel ratio (A/F)b becomes the lowest at the time of an acceleration operation. At this time, if the amplitude ΔH of the hydrocarbon concentration is about 200 ppm, it is possible to remove the NO_x well. The base air-fuel ratio (A/F)b is normally larger than the time of acceleration operation. Therefore, as shown in FIG. **14**, if the amplitude ΔH of the hydrocarbon concentration is 200 ppm or more, an excellent NO_x purification rate can be obtained.

On the other hand, it is learned that when the base air-fuel ratio (A/F)b is the highest, if making the amplitude ΔH of the hydrocarbon concentration 10000 ppm or so, an excellent NO_x purification rate is obtained. Further, if the amplitude ΔH of the hydrocarbon concentration is over 10000 ppm, there is the danger that the air-fuel ratio (A/F)in will become rich. Therefore, there is the danger of the first NO_x purification method no longer being able to be performed. Therefore, in the present invention, the predetermined range of the amplitude of the hydrocarbon concentration is made 200 ppm to 10000 ppm.

Further, if the vibration period ΔT of the hydrocarbon concentration becomes longer, the oxygen concentration around the active NO_2* becomes higher in the time after the hydrocarbons are fed to when the hydrocarbons are next fed. In this case, if the vibration period ΔT of the hydrocarbon concentration becomes longer than about 5 seconds, the active NO_2* starts to be absorbed in the form of nitrates inside the basic layer **53**. Therefore, as shown in FIG. **15**, if the vibration period ΔT of the hydrocarbon concentration becomes longer than about 5 seconds, the NO_x purification rate falls. Therefore, the vibration period ΔT of the hydrocarbon concentration has to be made 5 seconds or less.

On the other hand, if the vibration period ΔT of the hydrocarbon concentration becomes about 0.3 second or less, the fed hydrocarbons start to build up on the exhaust gas flow surface of the exhaust purification catalyst **13**, therefore, as shown in FIG. **15**, if the vibration period ΔT of the hydrocarbon concentration becomes about 0.3 second or less, the NO_x purification rate falls. Therefore, in the present invention, the vibration period of the hydrocarbon concentration is made from 0.3 second to 5 seconds.

Now, in this embodiment according to the present invention, by changing the injection amount and injection timing of hydrocarbons from the hydrocarbon feed valve **16**, the amplitude ΔH and vibration period ΔT of the hydrocarbon concentration are controlled so as to become the optimum values in accordance with the engine operating state. FIG. **16** and FIG. **17** show the changes in the optimum hydrocarbon concentration in accordance with the engine operating state and the injection amounts of hydrocarbons W from the hydrocarbon feed valve **16** causing these. Note that, FIG. **16** shows the case where the base air-fuel ratio (A/F)b is changed, while FIG. **17** shows the case where the intake air amount GA, that is, exhaust gas amount, is changed.

As explained above, to remove the NO_x well, as shown in FIG. **16**, the amplitude of the hydrogen concentration has to be increased as the base air-fuel ratio (A/F)b becomes higher. To make the amplitude of the hydrocarbon concentration larger, it is necessary to increase the injection amount of hydrocarbons W. Therefore, in this embodiment according to the present invention, the higher the base air-fuel ratio (A/F)b, the greater the injection amount of hydrocarbons W is made.

On the other hand, when the base air-fuel ratio (A/F)b is constant and under this a certain amount of hydrocarbons is fed, if the intake air amount GA increases, that is, if the exhaust gas amount increases, the hydrogen concentration in the exhaust gas will fall. In this case, to maintain the hydrogen concentration in the exhaust gas at a constant concentration regardless of the intake air amount GA, it is necessary that the hydrocarbon feed amount be increased as the intake air amount GA increases. Therefore, in this embodiment according to the present invention, as shown in FIG. **17**, the more the intake air amount GA increases, the more the injection amount of hydrocarbons W is increased.

The injection amount of hydrocarbons W enabling the change of the optimum concentration of hydrocarbons in accordance with the engine operating state to be obtained in this way changes in accordance with the operating state of the engine. In this embodiment according to the present invention, the injection amount of hydrocarbons W is stored as a function of the demanded torque TQ of the engine and the engine speed N in the form of a map such as shown in FIG. **18** in advance in the ROM **32**.

FIG. **19** shows the NO_x purification rate when feeding aqueous urea solution sufficient for reducing the NO_x which is contained in exhaust gas from the aqueous urea solution feed valve **17** and reducing the NO_x which is contained in the exhaust gas at the NO_x selective reduction catalyst **15**. As will be understood from FIG. **19**, this NO_x selective reduction catalyst **15** becomes activated resulting in the NO_x purification rate becoming higher if the temperature of the NO_x selective reduction catalyst **15** exceeds about 200° C. The NO_x purification method which uses the ammonia produced from the aqueous urea solution in this way to reduce the NO_x which is contained in exhaust gas at the NO_x selective reduction catalyst **15** will be referred to as the second NO_x purification method below.

When using the first NO_x purification method, as shown in FIG. **5**, even if the temperature of the exhaust purification catalyst **13** becomes high, a high NO_x purification rate can be obtained. On the other hand, the aqueous urea solution cannot be resupplied just anywhere, so it is preferable not to use the aqueous urea solution as much as possible. Therefore, in the present invention, usually, the first NO_x purification method is used for an NO_x purification action. However, as will be understood from FIG. **16** and FIG. **17**, the leaner the base air-fuel ratio (A/F)b becomes, the more the hydrocarbon injection amount W increases, while the greater the intake air amount GA, the more the hydrocarbon injection amount W increases. In this case, if the hydrocarbon injection amount W extremely increases, the amount of consumption of hydrocarbons increases. In this case, it is preferable to use the second NO_x purification method.

Therefore, in the present invention, usually, the first NO_x purification method is used. When a representative value representing the amount of hydrocarbons which is consumed for purification of NO_x by the first NO_x purification method exceeds a predetermined allowable value, the second NO_x purification method which uses the ammonia derived from the fed urea to reduce the NO_x contained in the exhaust gas in the NO_x selective reduction catalyst **15** is used.

As this representative value, it is possible to use the injection amount per injection of hydrocarbons fed for purification of NO_x by the first NO_x purification method. Further, as this representative value, it is also possible to use the oxygen concentration in the exhaust gas. Of course, as this representative value, it is also possible to use other values expressing the amount of consumption of hydrocarbons.

In this regard, the NO_x selective reduction catalyst **15** which is used in the embodiments of the present invention is weak in oxidizing strength of hydrocarbons. Therefore, even if hydrocarbons flow into the NO_x selective reduction catalyst **15**, it cannot be expected that the heat of the oxidation reaction of the hydrocarbons can be used to make the temperature of the NO_x selective reduction catalyst **15** rise. Therefore, in this embodiment according to the present invention, when the NO_x selective reduction catalyst **15** should be raised in temperature, hydrocarbons are fed from the hydrocarbon feed valve **16** and the heat of oxidation reaction of the hydrocarbons at the exhaust purification catalyst **13** is used to raise the exhaust gas temperature and thereby raise the temperature of the NO_x selective reduction catalyst **15**.

Now, the temperature of the NO_x selective reduction catalyst **15** differs depending on the position of attachment of the NO_x selective reduction catalyst **15**, but, for example, if arranging the exhaust purification catalyst **13** at the outlet of the exhaust turbine **7***b* and arranging the NO_x selective reduction catalyst **15** far from the exhaust purification catalyst **13** under the floor of the vehicle, the temperature of the NO_x selective reduction catalyst **15** becomes about 100° C. lower than the temperature of the exhaust purification catalyst **13**.

On the other hand, when the first NO_x purification method is being used, the exhaust purification catalyst **13** usually becomes 300° C. or more. Therefore, at this time, the NO_x selective reduction catalyst **15** becomes 200° C. or more. As will be understood from FIG. **19**, if the NO_x selective reduction catalyst **15** becomes 200° C. or more, it becomes activated. Therefore, when the first NO_x purification method is being used, usually the NO_x selective reduction catalyst **15** is activated.

As opposed to this, if the NO_x purification method is switched from the first NO_x purification method to the second NO_x purification method and, at this time, the feed of hydrocarbons is stopped, the NO_x selective reduction catalyst **15** gradually falls in temperature. Therefore, in this embodiment according to the present invention, at this time, hydrocarbons are fed from the hydrocarbon feed valve **16** so that the NO_x selective reduction catalyst **15** will not be deactivated. At this time, the amount of hydrocarbons required for maintaining the NO_x selective reduction catalyst **15** in the activated state is found in advance by experiments. When the second NO_x purification method is used for the NO_x purification action, the amount of hydrocarbons found by this experiment is fed.

FIG. **20**A and FIG. **20**B show examples of the injection amount WH and the injection interval ΔT of hydrocarbons found by experiments required for maintaining the NO_x selective reduction catalyst **15** in the active state when the second NO_x purification method is being used. In this example, as shown in FIG. **20**A, the injection amount WH and injection interval ΔT of hydrocarbons are functions of a temperature representing the temperature of the exhaust purification catalyst **13**, for example, the temperature TB of the exhaust purification catalyst **13** and the injection amount WH and the injection interval ΔT of hydrocarbons increase the higher the temperature of the exhaust purification catalyst **13**.

On the other hand, in this example, as shown in FIG. **20**B, the injection amount WH and injection interval ΔT of hydrocarbons are a value representing the oxygen concentration in the exhaust gas, for example, the air-fuel ratio. The injection amount WH and the injection interval ΔT of hydrocarbons become greater the leaner the air-fuel ratio. The relationship between the injection amount WH and catalyst temperature TB and the air-fuel ratio A/F and the relationship between the injection interval ΔT and catalyst temperature TB and the air-fuel ratio A/F shown in FIG. **20**A and FIG. **20**B are respectively stored in the form of maps such as shown in FIG. **21**A and FIG. **21**B in advance in the ROM **32**.

Note that, in this case, it is also possible to control just one of the injection amount WH and injection interval ΔT to maintain the NO_x selective reduction catalyst **15** in the active state. Therefore, if considering this case as well, in this embodiment according to the present invention, one or both of the injection amount WH and injection interval ΔT of hydrocarbons which are fed when the second NO_x purification method is used for the NO_x purification action are stored in advance as functions of the temperature TB representing the temperature of the exhaust purification catalyst **13** and the value representing the oxygen concentration in the exhaust gas.

FIG. **22** shows a first embodiment of an exhaust purification processing routine. This routine is executed by interruption every predetermined time.

In this embodiment, when the representative value representing the amount of hydrocarbons which is consumed for removing the NO_x by the first NO_x purification method exceeds a predetermined allowable value, the NO_x purification method is switched from the first NO_x purification method to the second NO_x purification method regardless of whether the NO_x selective reduction catalyst is activated. That is, in this embodiment, if the exhaust purification catalyst **13** is activated, normally it is considered that the NO_x selective reduction catalyst **15** is also activated and the switching action of the NO_x purification method is performed.

That is, referring to FIG. **22**, first, at step **100**, the injection amount W of hydrocarbons is calculated from the map shown in FIG. **18**. Next, at step **101**, it is judged if the above representative value, for example, the injection amount of hydrocarbons W, exceeds the allowable value W_0. When $W \leq W_0$, the routine proceeds to step **102** where hydrocarbons are injected from the hydrocarbon feed valve **16** in accordance with the injection amount W calculated at step **100** and a predetermined injection interval. At this time, the purification action of the NO_x which is contained in the exhaust gas is performed by the first NO_x purification method.

As opposed to this, when it is judged at step **101** that $W > W_0$, the routine proceeds to step **103** where the second

NO_x purification method is used for the purification action of the NO_x which is contained in the exhaust gas. That is, at step **103** and at step **104**, the injection amount WH and injection interval ΔT of hydrocarbons are respectively calculated from the maps shown in FIG. **21**A and FIG. **21**B, next, at step **105**, hydrocarbons are injected from the hydrocarbon feed valve **16** in accordance with the injection amount WH and injection interval ΔT required for maintaining the NO_x selective reduction catalyst **15** in the active state. Next, at step **106**, the feed amount of the aqueous urea solution required for reducing the NO_x which is contained in the exhaust gas is calculated, next, at step **107**, the calculated amount of aqueous urea solution is fed from the aqueous urea solution feed valve **17**.

FIG. **23** shows a second embodiment of an exhaust purification processing routine. This routine is also executed by interruption every certain time.

In this embodiment, when the representative value representing the amount of hydrocarbons which is consumed for removal of NO_x by the first NO_x purification method exceeds a predetermined allowable value, if the NO_x selective reduction catalyst **15** is activated, the NO_x purification method is switched from the first NO_x purification method to the second NO_x purification method. That is, in this embodiment, when the above representative value exceeds the above allowable value, if the NO_x selective reduction catalyst **15** is not activated, the NO_x purification action by the first NO_x purification method is continued. When the NO_x selective reduction catalyst **15** is later activated, at that time, the NO_x purification method is switched from the first NO_x, purification method to the second NO_x purification method.

That is, referring to FIG. **23**, first, at step **200**, the injection amount W of hydrocarbons is calculated from the map shown in FIG. **18**. Next, at step **201**, it is judged if the above representative value, for example, the injection amount W of hydrocarbons, exceeds the allowable value W_0. When $W \le W_0$, the routine proceeds to step **202** where hydrocarbons are fed from the hydrocarbon feed valve **16** in accordance with the injection amount W calculated at step **200** and a predetermined injection interval. At this time, the purification action of the NO_x which is contained in the exhaust gas is performed by the first NO_x purification method.

As opposed to this, when it is judged at step **201** that $W > W_0$, the routine proceeds to step **203** where it is judged if the temperature TC of the NO_x, selective reduction catalyst **15** exceeds the activation temperature TCX, for example, 200° C. When TC≤TCX, that is, when the NO_x selective reduction catalyst **15** is not activated, the routine proceeds to step **202** where the purification action of the NO_x, in the exhaust gas is performed by the first NO_x purification method.

As opposed to this, when it is judged at step **203** that TC>TCX, that is, when the NO_x selective reduction catalyst **15** is activated, the routine proceeds to step **204** where the purification action of NO_x which is contained in exhaust gas is performed by the second NO_x purification method. That is, at step **204** and at step **205**, the injection amount WH and injection interval ΔT of hydrocarbons are respectively calculated from the maps shown in FIG. **21**A and FIG. **21**B, next, at step **206**, hydrocarbons are injected from the hydrocarbon feed valve **16** in accordance with the injection amount WH and injection interval ΔT required for maintaining the NO_x selective reduction catalyst **15** in the activated state. Next, at step **207**, the feed amount of the aqueous urea solution required for reducing the NO_x which is contained in the exhaust gas is calculated, next, at step **208**, this calculated amount of aqueous urea solution is fed from the aqueous urea solution feed valve **17**.

FIG. **24** and FIG. **25** show a third embodiment. In the embodiment shown in FIG. **1**, when the injection amount of hydrocarbons increases for performing the first NO_x purification method, if the action of increasing the injection amount of hydrocarbons continues, sometimes there is a danger that the exhaust purification catalyst **13** will clog or thermally degrade. When there is such a danger, it is necessary to stop the purification of NO_x by the first NO_x purification method.

Therefore, in this embodiment, the state of the engine and exhaust purification catalyst **13** where the purification of NO_x by the first NO_x purification method should be stopped is set in advance. When the engine and exhaust purification catalyst **13** become this state, the exhaust purification method is switched from the first NO_x purification method to the second NO_x purification method. As an example of such a state, there is the time when there is the danger of the exhaust purification catalyst **13** clogging or there is the danger of the exhaust purification catalyst **13** thermally degrading.

FIG. **24** shows the region in which there is the danger of the mainly upstream end of the exhaust purification catalyst **13** clogging by DZ in the 3D space of the injection amount W of hydrocarbons, the temperature TB of the exhaust purification catalyst **13**, and the intake air amount QA as the xyz axes. That is, when the injection amount W is large, the temperature TB of the exhaust purification catalyst **13** is low, and the intake air amount QA is small, the fed hydrocarbons easily pool at the upstream end of the exhaust purification catalyst **13** in a liquid state, therefore there is the danger that the exhaust purification catalyst **13** will become clogged. Therefore, in this embodiment, when the engine and exhaust purification catalyst **13** are in the region DZ shown in FIG. **24**, the NO_x purification action by the first NO_x purification method is stopped.

On the other hand, if the injection amount W of hydrocarbons increases and the heat of oxidation reaction of the hydrocarbons causes the temperature TB of the exhaust purification catalyst **13** to become extremely high, there is the danger that the exhaust purification catalyst **13** will degrade due to heat. Therefore, in this embodiment, when the temperature TB of the exhaust purification catalyst **13** reaches the limit temperature TBX causing thermal degradation, the NO_x purification action by the first NO_x purification method is stopped. Note that, in this embodiment, while the NO_x purification method by the first NO_x purification method is stopped, the hydrocarbons required for maintaining the NO_x selective reduction catalyst **15** in the activated state are fed from the hydrocarbon feed valve **16**.

FIG. **25** shows a processing routine for exhaust purification for working a third embodiment. This routine is also executed by interruption every certain time.

Referring to FIG. **25**, first, at step **300**, it is judged if the state of the engine and exhaust purification catalyst **13** is within the region DZ shown in FIG. **24**. When the state of the engine and exhaust purification catalyst **13** is not within the region DZ shown in FIG. **24**, the routine proceeds to step **301** where it is judged if the temperature TB of the exhaust purification catalyst **13** becomes higher than the limit temperature TBX causing thermal degradation. When TB≤TBX, the routine proceeds to step **302**.

At step **302**, the injection amount W of hydrocarbons is calculated from the map shown in FIG. **18**. Next, at step **303**, it is judged if the above-mentioned representative value, for example, the injection amount W of hydrocarbons, exceeds the allowable value W_0. When $W \le W_0$, the routine proceeds to step **304** where hydrocarbons are fed from the hydrocarbon feed valve **16** is accordance with the injection amount W calculated at step **302** and a predetermined injection interval.

At this time, the purification action of the NO_x contained in the exhaust gas is performed by the first NO_x purification method.

As opposed to this, when, at step **303**, it is judged that $W>W_0$, the routine proceeds to step **305** where it is judged if the temperature TC of the NO_x selective reduction catalyst **15** exceeds the activation temperature TCX, for example, 200° C. When TC≤TCX, that is, when the NO_x selective reduction catalyst **15** is not activated, the routine proceeds to step **304** where the first NO_x purification method is used for the purification action of the NO_x in the exhaust gas.

As opposed to this, when it is judged at step **305** that TC>TCX, that is, when the NO_x selective reduction catalyst **15** is activated, the routine proceeds to step **306** where the second NO_x purification method is used for the purification action of the NO_x which is contained in the exhaust gas. That is, at step **306** and at step **307**, the injection amount WH and injection interval ΔT of hydrocarbons are calculated from the maps shown in FIG. **21**A and FIG. **21**B, next, at step **308**, hydrocarbons are injected from the hydrocarbon feed valve **16** in accordance with these injection amount WH and injection interval ΔT required for maintaining the NO_x selective reduction catalyst **15** in the activated state. Next, at step **309**, the feed amount of the aqueous urea solution required for reducing the NO_x which is contained in the exhaust gas is calculated, next, at step **310**, this calculated amount of aqueous urea solution is fed from the aqueous urea solution feed valve **17**.

On the other hand, when it is judged at step **300** that the states of the engine and exhaust purification catalyst **13** are within the region DZ shown in FIG. **24** or when it is judged at step **301** that TB>TBX, the routine proceeds to step **306**, and the NO_x purification method is switched from the first NO_x purification method to the second NO_x purification method.

REFERENCE SIGNS LIST

4 . . . intake manifold
5 . . . exhaust manifold
7 . . . exhaust turbocharger
12 . . . exhaust pipe
13 . . . exhaust purification catalyst
15 . . . NO_x selective reduction catalyst
16 . . . hydrocarbon feed valve
17 . . . aqueous urea solution feed valve

The invention claimed is:

1. An exhaust purification system of an internal combustion engine comprising:

an engine exhaust passage;

an exhaust purification catalyst for reacting NO_x contained in exhaust gas and reformed hydrocarbons arranged inside of the engine exhaust passage;

a urea feeding device arranged inside of the engine exhaust passage downstream of the exhaust purification catalyst;

an NO_x selective reduction catalyst able to reduce NO_x using ammonia derived from urea fed from the urea feeding device arranged inside of the engine exhaust passage downstream of the exhaust purification catalyst;

a precious metal catalyst carried on an exhaust gas flow surface of the exhaust purification catalyst;

a basic exhaust gas flow surface part formed around the precious metal catalyst; and

an electronic control unit, wherein the electronic control unit is configured to control a vibration of a concentration of hydrocarbons flowing into the exhaust purification catalyst within a predetermined range of amplitude and within a predetermined range of period, and is configured to control the vibration period of the hydrocarbon concentration longer than the predetermined range of period, wherein

when the electronic control unit controls the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period, the exhaust purification catalyst has a property of producing a reducing intermediate containing nitrogen and hydrocarbons that chemically reduces the NO_x contained in the exhaust by a reducing action of the produced reducing intermediate, and the exhaust purification catalyst chemically reduces the NO_x that is contained in exhaust gas without storing, or storing a fine amount of nitrates in the basic exhaust gas flow surface part,

when the electronic control unit controls the vibration period of the hydrocarbon concentration longer than the predetermined range of period, the exhaust purification catalyst has a property of being increased in storage amount of NO_x that is contained in exhaust gas, and

when a representative value representing an amount of hydrocarbons that is consumed for removal of NO_x when the electronic control unit is controlling the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period exceeds a predetermined allowable value, the electronic control unit is configured to cause the urea feeding device to feed urea to the exhaust as to reduce NO_x contained in exhaust gas at the NO_x selective reduction catalyst.

2. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein a state of the engine and exhaust purification catalyst at which the electronic control unit stops controlling the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period is set in advance, and wherein when the engine and exhaust purification catalyst become the set state, the electronic control unit is configured to stop controlling the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period, and is configured cause the urea feeding device to feed urea to the exhaust gas to reduce NO_x contained in exhaust gas at the NO_x selective reduction catalyst.

3. The exhaust purification system of an internal combustion engine as claimed in claim **2**, wherein the state set in advance is when there is a danger of the exhaust purification catalyst becoming clogged, or when there is a danger of the exhaust purification catalyst becoming thermally degraded.

4. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein the representative value is an injection amount per injection of hydrocarbons that are fed when the electronic control unit is controlling the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period.

5. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein the representative value is an oxygen concentration in the exhaust gas.

6. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein when the electronic control unit is causing the urea feeding device to feed urea to the exhaust gas to reduce NO_x contained in exhaust gas at the NO_x selective reduction catalyst, the electronic control unit is configured to cause the feeding of an amount of hydrocarbons that is necessary for maintaining the NO_x selective reduction catalyst in an activated state.

7. The exhaust purification system of an internal combustion engine as claimed in claim **6**, wherein one of, or both of, an injection amount of, and/or injection interval of, hydrocarbons that are fed when the electronic control unit is causing the urea feeding device to feed urea to the exhaust gas to reduce NO_x contained in exhaust gas at the NO_x selective reduction catalyst is stored in advance as a function of a temperature representing a temperature of the exhaust purification catalyst and a value representing an oxygen concentration in the exhaust gas.

8. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein when the representative value exceeds the predetermined allowable value, if the NO_x selective reduction catalyst is not activated, the electronic control unit is configured to continue controlling the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period.

9. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein NO_x contained in exhaust gas and reformed hydrocarbons react in the exhaust purification catalyst to produce the reducing intermediate containing nitrogen and hydrocarbons, and wherein the predetermined vibration period of the hydrocarbon concentration is the vibration period necessary for continued production of the reducing intermediate.

10. The exhaust purification system of an internal combustion engine as claimed in claim **9**, wherein the predetermined vibration period of the hydrocarbon concentration is from 0.3 seconds to 5 seconds.

11. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein when the representative value exceeds the predetermined allowable value, the electronic control unit is configured to cause the urea feeding device to feed urea to the exhaust gas regardless of whether the NO_x selective reduction catalyst is activated.

12. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein when the representative value exceeds the predetermined allowable value, the electronic control unit is configured to cause the urea feeding device to feed urea to the exhaust gas if the NO_x selective reduction catalyst is activated.

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